CHEMISTRY - THE CENTRAL SCIENCE



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Chemistry - The Central Science

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1: INTRODUCTION - MATTER AND MEASUREMENT

Chemistry is the study of matter and the changes that material substances undergo. Of all the scientific disciplines, it is perhaps the most extensively connected to other fields of study. As you begin your study of college chemistry, those of you who do not intend to become professional chemists may well wonder why you need to study chemistry. You will soon discover that a basic understanding of chemistry is useful in a wide range of disciplines and career paths. You will also discover that an understanding of chemistry helps you make informed decisions about many issues that affect you, your community, and your world. A major goal of this text is to demonstrate the importance of chemistry in your daily life and in our collective understanding of both the physical world we occupy and the biological realm of which we are a part.

1.1: Studying Chemistry

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1.1: Studying Chemistry

Learning Objectives

- To recognize the breadth, depth, and scope of chemistry.

Chemistry is the study of matter and the changes that material substances undergo. Of all the scientific disciplines, it is perhaps the most extensively connected to other fields of study. Geologists who want to locate new mineral or oil deposits use chemical techniques to analyze and identify rock samples. Oceanographers use chemistry to track ocean currents, determine the flux of nutrients into the sea, and measure the rate of exchange of nutrients between ocean layers. Engineers consider the relationships between the structures and the properties of substances when they specify materials for various uses. Physicists take advantage of the properties of substances to detect new subatomic particles. Astronomers use chemical signatures to determine the age and distance of stars and thus answer questions about how stars form and how old the universe is. The entire subject of environmental science depends on chemistry to explain the origin and impacts of phenomena such as air pollution, ozone layer depletion, and global warming.

The disciplines that focus on living organisms and their interactions with the physical world rely heavily on **biochemistry**, the application of chemistry to the study of biological processes. A living cell contains a large collection of complex molecules that carry out thousands of chemical reactions, including those that are necessary for the cell to reproduce. Biological phenomena such as vision, taste, smell, and movement result from numerous chemical reactions. Fields such as medicine, pharmacology, nutrition, and toxicology focus specifically on how the chemical substances that enter our bodies interact with the chemical components of the body to maintain our health and well-being. For example, in the specialized area of sports medicine, a knowledge of chemistry is needed to understand why muscles get sore after exercise as well as how prolonged exercise produces the euphoric feeling known as “runner’s high.”

Examples of the practical applications of chemistry are everywhere (Figure 1.1.1). Engineers need to understand the chemical properties of the substances when designing biologically compatible implants for joint replacements or designing roads, bridges, buildings, and nuclear reactors that do not collapse because of weakened structural materials such as steel and cement. Archaeology and paleontology rely on chemical techniques to date bones and artifacts and identify their origins. Although law is not normally considered a field related to chemistry, forensic scientists use chemical methods to analyze blood, fibers, and other evidence as they investigate crimes. In particular, DNA matching—comparing biological samples of genetic material to see whether they could have come from the same person—has been used to solve many high-profile criminal cases as well as clear innocent people who have been wrongly accused or convicted. Forensics is a rapidly growing area of applied chemistry. In addition, the proliferation of chemical and biochemical innovations in industry is producing rapid growth in the area of patent law. Ultimately, the dispersal of information in all the fields in which chemistry plays a part requires experts who are able to explain complex chemical issues to the public through television, print journalism, the Internet, and popular books.

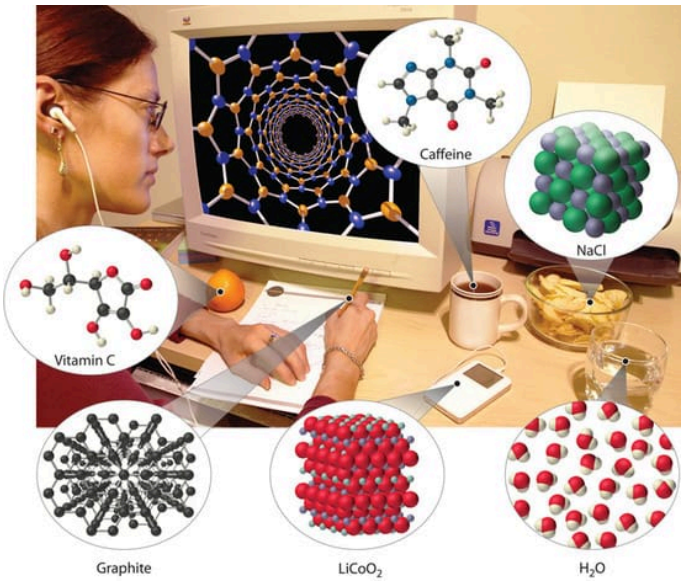


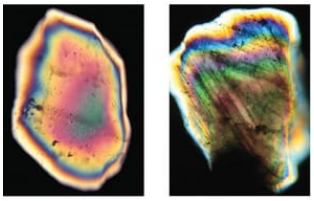
Figure 1.1.1: Chemistry in Everyday Life. Although most people do not recognize it, chemistry and chemical compounds are crucial ingredients in almost everything we eat, wear, and use.

A woman taking down notes while looking at a computer screen with various things around her desk. The chemical compounds which make up these items are highlighted with magnifying pointers. The chemical compounds are caffeine in cup of coffee, N a C l in bowl of chips, H 2 O in glass of water, L i C o O 2 in iPod, Graphite in notepad, Vitamin C in orange.

By this point, it shouldn't surprise you to learn that chemistry was essential in explaining a pivotal event in the history of Earth: the disappearance of the dinosaurs. Although dinosaurs ruled Earth for more than 150 million years, fossil evidence suggests that they became extinct rather abruptly approximately 66 million years ago. Proposed explanations for their extinction have ranged from an epidemic caused by some deadly microbe or virus to more gradual phenomena such as massive climate changes. In 1978 Luis Alvarez (a Nobel Prize–winning physicist), the geologist Walter Alvarez (Luis's son), and their coworkers discovered a thin layer of sedimentary rock formed 66 million years ago that contained unusually high concentrations of iridium, a rather rare metal (part (a) in Figure 1.1.2). This layer was deposited at about the time dinosaurs disappeared from the fossil record. Although iridium is very rare in most rocks, accounting for only 0.00000001% of Earth's crust, it is much more abundant in comets and asteroids. Because corresponding samples of rocks at sites in Italy and Denmark contained high iridium concentrations, the Alvarezes suggested that the impact of a large asteroid with Earth led to the extinction of the dinosaurs. When chemists analyzed additional samples of 66-million-year-old sediments from sites around the world, all were found to contain high levels of iridium. In addition, small grains of quartz in most of the iridium-containing layers exhibit microscopic cracks characteristic of high-intensity shock waves (part (b) in Figure 1.1.2). These grains apparently originated from terrestrial rocks at the impact site, which were pulverized on impact and blasted into the upper atmosphere before they settled out all over the world.



(a)



(b)

Figure 1.1.2: Evidence for the Asteroid Impact That May Have Caused the Extinction of the Dinosaurs. (a) Luis and Walter Alvarez are standing in front of a rock formation in Italy that shows the thin white layer of iridium-rich clay deposited at the time the dinosaurs became extinct. The concentration of iridium is 30 times higher in this layer than in the rocks immediately above and below it. There are no significant differences between the clay layer and the surrounding rocks in the concentrations of any of the 28 other elements examined. (b) Microphotographs of an unshocked quartz grain (left) and a quartz grain from the iridium-rich layer exhibiting microscopic cracks resulting from shock (right).

Scientists calculate that a collision of Earth with a stony asteroid about 10 kilometers (6 miles) in diameter, traveling at 25 kilometers per second (about 56,000 miles per hour), would almost instantaneously release energy equivalent to the explosion of about 100 million megatons of TNT (trinitrotoluene). This is more energy than that stored in the entire nuclear arsenal of the world. The energy released by such an impact would set fire to vast areas of forest, and the smoke from the fires and the dust created by the impact would block the sunlight for months or years, eventually killing virtually all green plants and most organisms that depend on them. This could explain why about 70% of all species—not just dinosaurs—disappeared at the same time. Scientists also calculate that this impact would form a crater at least 125 kilometers (78 miles) in diameter. Recently, satellite images from a Space Shuttle mission confirmed that a huge asteroid or comet crashed into Earth's surface across the Yucatan's northern tip in the Gulf of Mexico 65 million years ago, leaving a partially submerged crater 180 kilometers (112 miles) in diameter (Figure 1.1.3). Thus simple chemical measurements of the abundance of one element in rocks led to a new and dramatic explanation for the extinction of the dinosaurs. Though still controversial, this explanation is supported by additional evidence, much of it chemical.

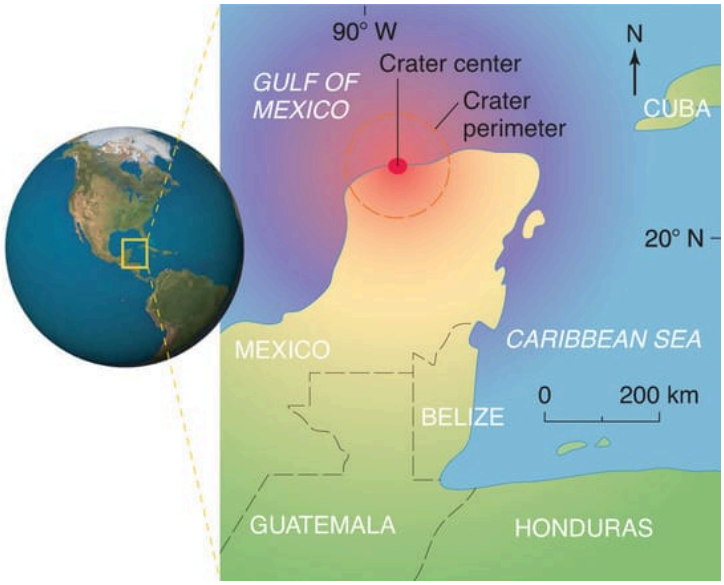


Figure 1.1.3: Asteroid Impact. The location of the asteroid impact crater near what is now the tip of the Yucatan Peninsula in Mexico.

This is only one example of how chemistry has been applied to an important scientific problem. Other chemical applications and

explanations that we will discuss in this text include how astronomers determine the distance of galaxies and how fish can survive in subfreezing water under polar ice sheets. We will also consider ways in which chemistry affects our daily lives: the addition of iodine to table salt; the development of more effective drugs to treat diseases such as cancer, AIDS (acquired immunodeficiency syndrome), and arthritis; the retooling of industry to use nonchlorine-containing refrigerants, propellants, and other chemicals to preserve Earth's ozone layer; the use of modern materials in engineering; current efforts to control the problems of acid rain and global warming; and the awareness that our bodies require small amounts of some chemical substances that are toxic when ingested in larger doses. By the time you finish this text, you will be able to discuss these kinds of topics knowledgeably, either as a beginning scientist who intends to spend your career studying such problems or as an informed observer who is able to participate in public debates that will certainly arise as society grapples with scientific issues.

Summary

An understanding of chemistry is essential for understanding much of the natural world and is central to many other disciplines. Chemistry is the study of matter and the changes material substances undergo. It is essential for understanding much of the natural world and central to many other scientific disciplines, including astronomy, geology, paleontology, biology, and medicine.

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1.2: Classification of Matter

Learning Objectives

- To classify matter.

Chemists study the structures, physical properties, and chemical properties of material substances. These consist of **matter**, which is anything that occupies space and has mass. Gold and iridium are matter, as are peanuts, people, and postage stamps. Smoke, smog, and laughing gas are matter. Energy, light, and sound, however, are not matter; ideas and emotions are also not matter.

The **mass** of an object is the quantity of matter it contains. Do not confuse an object's mass with its **weight**, which is a force caused by the gravitational attraction that operates on the object. Mass is a fundamental property of an object that does not depend on its location.In physical terms, the mass of an object is directly proportional to the force required to change its speed or direction. A more detailed discussion of the differences between weight and mass and the units used to measure them is included in Essential Skills 1 (Section 1.9). Weight, on the other hand, depends on the location of an object. An astronaut whose mass is 95 kg weighs about 210 lb on Earth but only about 35 lb on the moon because the gravitational force he or she experiences on the moon is approximately one-sixth the force experienced on Earth. For practical purposes, weight and mass are often used interchangeably in laboratories. Because the force of gravity is considered to be the same everywhere on Earth's surface, 2.2 lb (a weight) equals 1.0 kg (a mass), regardless of the location of the laboratory on Earth.

Under normal conditions, there are three distinct states of matter: solids, liquids, and gases. **Solids** are relatively rigid and have fixed shapes and volumes. A rock, for example, is a solid. In contrast, **liquids** have fixed volumes but flow to assume the shape of their containers, such as a beverage in a can. **Gases**, such as air in an automobile tire, have neither fixed shapes nor fixed volumes and expand to completely fill their containers. Whereas the volume of gases strongly depends on their temperature and **pressure** (the amount of force exerted on a given area), the volumes of liquids and solids are virtually independent of temperature and pressure. Matter can often change from one physical state to another in a process called a **physical change**. For example, liquid water can be heated to form a gas called steam, or steam can be cooled to form liquid water. However, such changes of state do not affect the chemical composition of the substance.

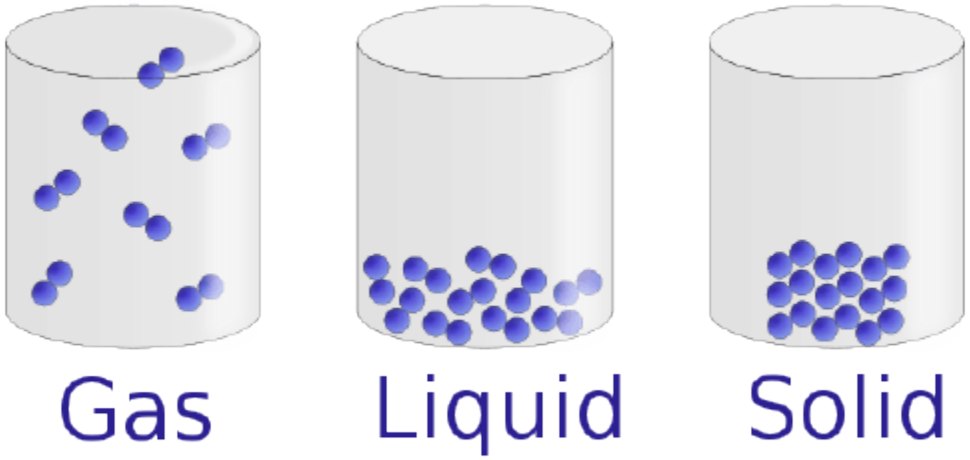


Figure 1.2.1: The Three States of Matter. Solids have a defined shape and volume. Liquids have a fixed volume but flow to assume the shape of their containers. Gases completely fill their containers, regardless of volume. Figure used with permission from Wikipedia

Pure Substances and Mixtures

A pure chemical substance is any matter that has a fixed chemical composition and characteristic properties. Oxygen, for example, is a pure chemical substance that is a colorless, odorless gas at 25°C. Very few samples of matter consist of pure

substances; instead, most are mixtures, which are combinations of two or more pure substances in variable proportions in which the individual substances retain their identity. Air, tap water, milk, blue cheese, bread, and dirt are all mixtures. If all portions of a material are in the same state, have no visible boundaries, and are uniform throughout, then the material is **homogeneous**. Examples of homogeneous mixtures are the air we breathe and the tap water we drink. Homogeneous mixtures are also called solutions. Thus air is a solution of nitrogen, oxygen, water vapor, carbon dioxide, and several other gases; tap water is a solution of small amounts of several substances in water. The specific compositions of both of these solutions are not fixed, however, but depend on both source and location; for example, the composition of tap water in Boise, Idaho, is not the same as the composition of tap water in Buffalo, New York. Although most solutions we encounter are liquid, solutions can also be solid. The gray substance still used by some dentists to fill tooth cavities is a complex solid solution that contains 50% mercury and 50% of a powder that contains mostly silver, tin, and copper, with small amounts of zinc and mercury. Solid solutions of two or more metals are commonly called alloys.

If the composition of a material is not completely uniform, then it is **heterogeneous** (e.g., chocolate chip cookie dough, blue cheese, and dirt). Mixtures that appear to be homogeneous are often found to be heterogeneous after microscopic examination. Milk, for example, appears to be homogeneous, but when examined under a microscope, it clearly consists of tiny globules of fat and protein dispersed in water. The components of heterogeneous mixtures can usually be separated by simple means. Solid-liquid mixtures such as sand in water or tea leaves in tea are readily separated by filtration, which consists of passing the mixture through a barrier, such as a strainer, with holes or pores that are smaller than the solid particles. In principle, mixtures of two or more solids, such as sugar and salt, can be separated by microscopic inspection and sorting. More complex operations are usually necessary, though, such as when separating gold nuggets from river gravel by panning. First solid material is filtered from river water; then the solids are separated by inspection. If gold is embedded in rock, it may have to be isolated using chemical methods.



Figure 1.2.2: A Heterogeneous Mixture. Under a microscope, whole milk is actually a heterogeneous mixture composed of globules of fat and protein dispersed in water. Figure used with permission from Wikipedia

Homogeneous mixtures (solutions) can be separated into their component substances by physical processes that rely on differences in some physical property, such as differences in their boiling points. Two of these separation methods are distillation and crystallization. **Distillation** makes use of differences in volatility, a measure of how easily a substance is converted to a gas at a given temperature. A simple distillation apparatus for separating a mixture of substances, at least one of which is a liquid. The most volatile component boils first and is condensed back to a liquid in the water-cooled condenser, from which it flows into the receiving flask. If a solution of salt and water is distilled, for example, the more volatile component, pure water, collects in the receiving flask, while the salt remains in the distillation flask.

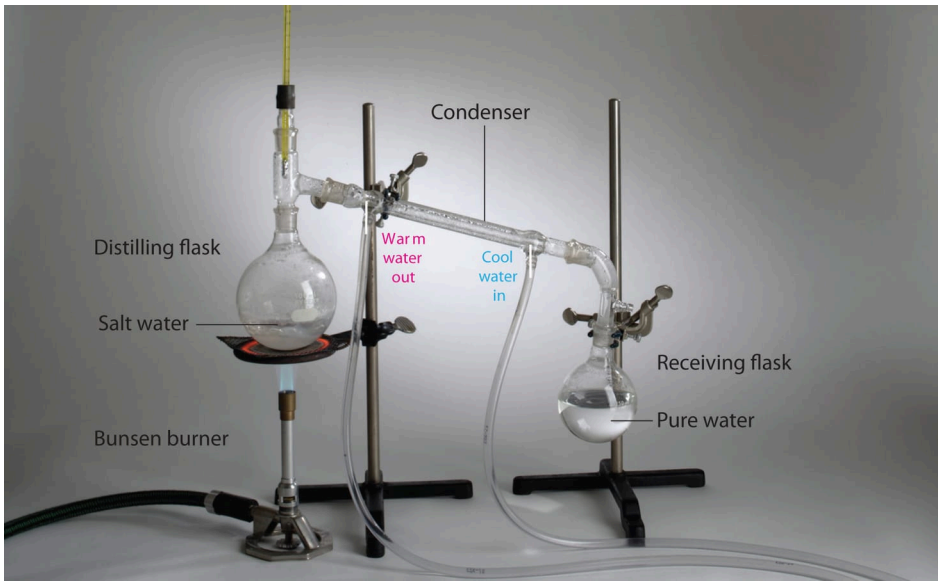


Figure 1.2.3: The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.

Mixtures of two or more liquids with different boiling points can be separated with a more complex distillation apparatus. One example is the refining of crude petroleum into a range of useful products: aviation fuel, gasoline, kerosene, diesel fuel, and lubricating oil (in the approximate order of decreasing volatility). Another example is the distillation of alcoholic spirits such as brandy or whiskey. (This relatively simple procedure caused more than a few headaches for federal authorities in the 1920s during the era of Prohibition, when illegal stills proliferated in remote regions of the United States!)

Crystallization separates mixtures based on differences in solubility, a measure of how much solid substance remains dissolved in a given amount of a specified liquid. Most substances are more soluble at higher temperatures, so a mixture of two or more substances can be dissolved at an elevated temperature and then allowed to cool slowly. Alternatively, the liquid, called the solvent, may be allowed to evaporate. In either case, the least soluble of the dissolved substances, the one that is least likely to remain in solution, usually forms crystals first, and these crystals can be removed from the remaining solution by filtration.



Figure 1.2.4: The Crystallization of Sodium Acetate from a Concentrated Solution of Sodium Acetate in Water. The addition of a small “seed” crystal (a) causes the compound to form white crystals, which grow and eventually occupy most of the flask. Video can be found here: www.youtube.com/watch?v=BLq5NibwV5g

closeup of bulb flask containing liquid with many thin spike crystals radially emerging from the center.

Most mixtures can be separated into pure substances, which may be either elements or compounds. An **element**, such as gray, metallic sodium, is a substance that cannot be broken down into simpler ones by chemical changes; a **compound**, such as white, crystalline sodium chloride, contains two or more elements and has chemical and physical properties that are usually different from those of the elements of which it is composed. With only a few exceptions, a particular compound has the same elemental composition (the same elements in the same proportions) regardless of its source or history. The chemical composition of a substance is altered in a process called a **chemical change**. The conversion of two or more elements, such as sodium and chlorine, to a chemical compound, sodium chloride, is an example of a chemical change, often called a chemical reaction. Currently, about 118 elements are known, but millions of chemical compounds have been prepared from these 118 elements. The known elements are listed in the periodic table.

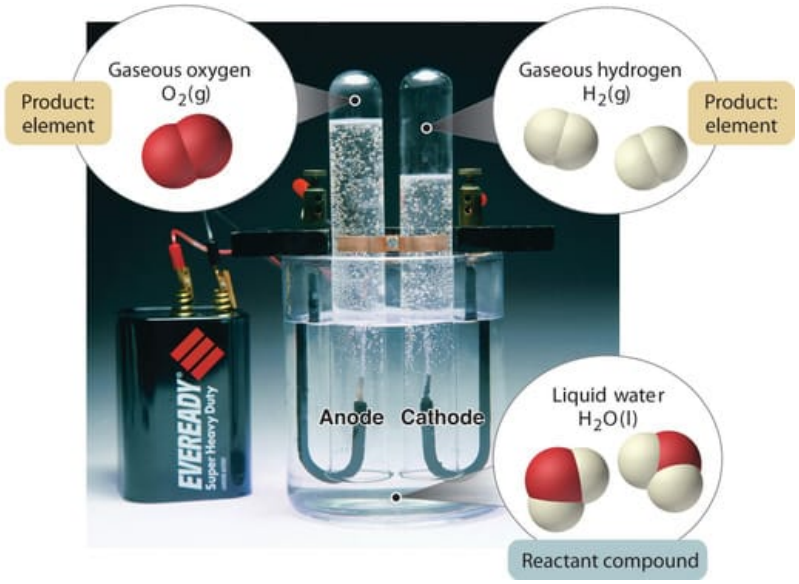


Figure 1.2.5: The Decomposition of Water to Hydrogen and Oxygen by Electrolysis. Water is a chemical compound; hydrogen and oxygen are elements.

a battery wired to an anode and cathode placed in a beaker filled with water. Two inverted test tubes are submerged in the water and placed over each of the electrodes to collect the gaseous products. Magnifying pointers show the molecular structure of water in the beaker as well as the hydrogen gas collected on the anode side and oxygen gas on the cathode side.

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In general, a reverse chemical process breaks down compounds into their elements. For example, water (a compound) can be decomposed into hydrogen and oxygen (both elements) by a process called electrolysis. In electrolysis, electricity provides the energy needed to separate a compound into its constituent elements (Figure 1.2.5). A similar technique is used on a vast scale to obtain pure aluminum, an element, from its ores, which are mixtures of compounds. Because a great deal of energy is required for electrolysis, the cost of electricity is by far the greatest expense incurred in manufacturing pure aluminum. Thus recycling aluminum is both cost-effective and ecologically sound.

The overall organization of matter and the methods used to separate mixtures are summarized in Figure 1.2.6.

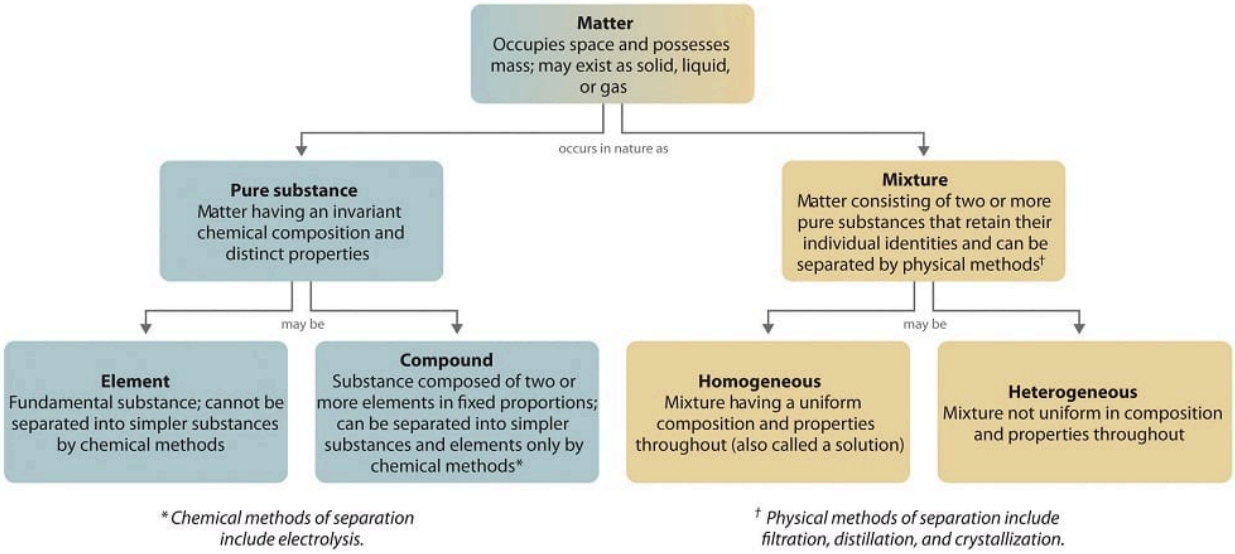


Figure 1.2.6: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

Example 1.2.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. filtered tea
b. freshly squeezed orange juice
c. a compact disc
d. aluminum oxide, a white powder that contains a 2:3 ratio of aluminum and oxygen atoms
e. selenium

Given: a chemical substance

Asked for: its classification

Strategy:

A. Decide whether a substance is chemically pure. If it is pure, the substance is either an element or a compound. If a substance can be separated into its elements, it is a compound.
B. If a substance is not chemically pure, it is either a heterogeneous mixture or a homogeneous mixture. If its composition is uniform throughout, it is a homogeneous mixture.

Solution

a. **A** Tea is a solution of compounds in water, so it is not chemically pure. It is usually separated from tea leaves by filtration. **B** Because the composition of the solution is uniform throughout, it is a homogeneous mixture.
b. **A** Orange juice contains particles of solid (pulp) as well as liquid; it is not chemically pure. B Because its composition is not uniform throughout, orange juice is a heterogeneous mixture.
c. **A** A compact disc is a solid material that contains more than one element, with regions of different compositions visible along its edge. Hence a compact disc is not chemically pure. **B** The regions of different composition indicate that a compact disc is a heterogeneous mixture.
d. **A** Aluminum oxide is a single, chemically pure compound.

e. **A** Selenium is one of the known elements.

Exercise 1.2.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. white wine
b. mercury
c. ranch-style salad dressing
d. table sugar (sucrose)

Answer A available at the end of this section.

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Summary

Matter can be classified according to physical and chemical properties. Matter is anything that occupies space and has mass. The three states of matter are solid, liquid, and gas. A physical change involves the conversion of a substance from one state of matter to another, without changing its chemical composition. Most matter consists of mixtures of pure substances, which can be homogeneous (uniform in composition) or heterogeneous (different regions possess different compositions and properties). Pure substances can be either chemical compounds or elements. Compounds can be broken down into elements by chemical reactions, but elements cannot be separated into simpler substances by chemical means. The properties of substances can be classified as either physical or chemical. Scientists can observe physical properties without changing the composition of the substance, whereas chemical properties describe the tendency of a substance to undergo chemical changes (chemical reactions) that change its chemical composition. Physical properties can be intensive or extensive. Intensive properties are the same for all samples; do not depend on sample size; and include, for example, color, physical state, and melting and boiling points. Extensive properties depend on the amount of material and include mass and volume. The ratio of two extensive properties, mass and volume, is an important intensive property called density.

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Answers

Exercise 1.2.1

solution
element
heterogeneous mixture
compound

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1.3: Properties of Matter

Learning Objectives

- To separate physical from chemical properties and changes

All matter has physical and chemical properties. **Physical properties** are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). **Chemical properties** describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion. All samples of a pure substance have the same chemical and physical properties. For example, pure copper is always a reddish-brown solid (a physical property) and always dissolves in dilute nitric acid to produce a blue solution and a brown gas (a chemical property).

Physical properties can be extensive or intensive. **Extensive properties** vary with the amount of the substance and include mass, weight, and volume. **Intensive properties**, in contrast, do not depend on the amount of the substance; they include color, melting point, boiling point, electrical conductivity, and physical state at a given temperature. For example, elemental sulfur is a yellow crystalline solid that does not conduct electricity and has a melting point of 115.2 °C, no matter what amount is examined (Figure 1.3.1). Scientists commonly measure intensive properties to determine a substance's identity, whereas extensive properties convey information about the amount of the substance in a sample.

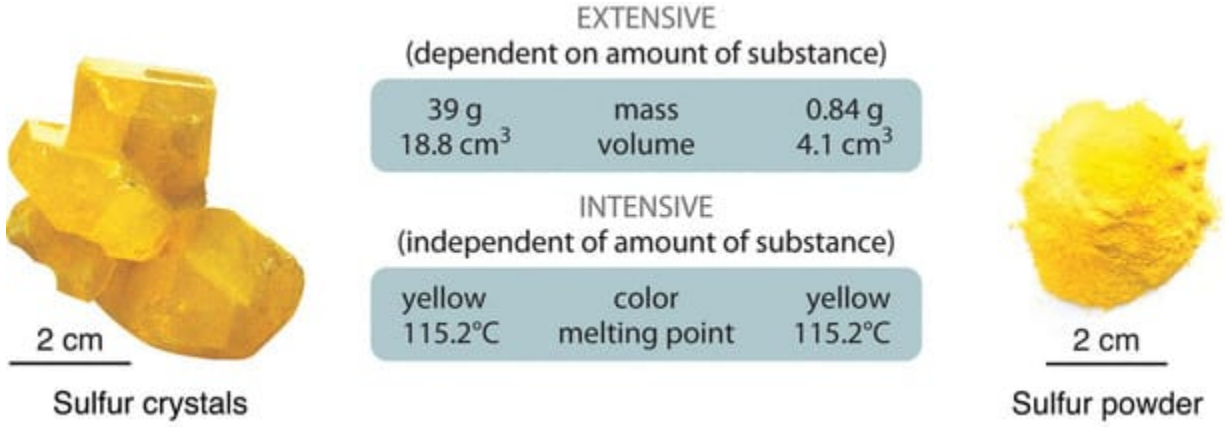


Figure 1.3.1: The Difference between Extensive and Intensive Properties of Matter. Because they differ in size, the two samples of sulfur have different extensive properties, such as mass and volume. In contrast, their intensive properties, including color, melting point, and electrical conductivity, are identical.

Although mass and volume are both extensive properties, their ratio is an important intensive property called **density** (ρ). Density is defined as mass per unit volume and is usually expressed in grams per cubic centimeter (g/cm^3). As mass increases in a given volume, density also increases. For example, lead, with its greater mass, has a far greater density than the same volume of air, just as a brick has a greater density than the same volume of Styrofoam. At a given temperature and pressure, the density of a pure substance is a constant:

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

$$\rho = \frac{m}{V}$$

Pure water, for example, has a density of 0.998 g/cm^3 at 25 °C. The average densities of some common substances are in Table 1.3.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float" (Figure 1.3.2).

Table 1.3.1: Densities of Common Substances

Substance	Density at 25 °C (g/cm^3)	Substance	Density at 25 °C (g/cm^3)
blood	1.035	corn oil	0.922
body fat	0.918	mayonnaise	0.910
whole milk	1.030	honey	1.420



Figure 1.3.2: Water and oil. Since the oil has a lower density than water, it floats on top. (CC-BY SA 3.0; Victor Blacus).

Physical Property and Change

Physical changes are changes in which no chemical bonds are broken or formed. This means that the same types of compounds or elements that were there at the beginning of the change are there at the end of the change. Because the ending materials are the same as the beginning materials, the properties (such as color, boiling point, etc) will also be the same. Physical changes involve moving molecules around, but not changing them. Some types of physical changes include:

- Changes of state (changes from a solid to a liquid or a gas and vice versa)
- Separation of a mixture
- Physical deformation (cutting, denting, stretching)
- Making solutions (special kinds of mixtures) .

As an ice cube melts, its shape changes as it acquires the ability to flow. However, its composition does not change. **Melting** is an example of a **physical change** (Figure 1.3.3), since some properties of the material change, but the identity of the matter does not. Physical changes can further be classified as reversible or irreversible. The melted ice cube may be refrozen, so melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolving is also a reversible physical change. When salt is dissolved into water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.



Figure 1.3.3: Ice Melting is a physical change. When solid water (H_2O) as ice melts into a liquid (water), it appears changed. However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass.

Chemical Properties and Change

Chemical changes occur when bonds are broken and/or formed between molecules or atoms. This means that one substance with a certain set of properties (such as melting point, color, taste, etc) is turned into a different substance with different properties. Chemical changes are frequently harder to reverse than physical changes.

One good example of a chemical change is burning paper. In contrast to the act of ripping paper, the act of burning paper actually results in the formation of new chemicals (carbon dioxide and water, to be exact). Another example of chemical change occurs when water is formed. Each molecule contains two atoms of hydrogen and one atom of oxygen chemically bonded.

Another example of a chemical change is what occurs when natural gas is burned in your furnace. This time, before the reaction we have a molecule of methane, CH_4, and two molecules of oxygen, O_2, while after the reaction we have two molecules of water, H_2O, and one molecule of carbon dioxide, CO_2. In this case, not only has the appearance changed, but the structure of the molecules has also changed. The new substances do not have the same chemical properties as the original ones. Therefore, this is a chemical change.

The combustion of magnesium metal is also chemical change (Magnesium + Oxygen → Magnesium Oxide):

$$2\,Mg + O_2 \rightarrow 2\,MgO$$

as is the rusting of iron (Iron + Oxygen → Iron Oxide/ Rust):

$$4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3$$

Using the components of composition and properties, we have the ability to distinguish one sample of matter from the others.

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1.4: Units of Measurement

Learning Objectives

- To identify the basic units of measurement of the seven fundamental properties
- Describe the names and abbreviations of the *SI base units* and the *SI decimal prefixes*.
- Define the *liter* and the *metric ton* in these units.
- Explain the meaning and use of *unit dimensions*; state the dimensions of *volume*.
- State the quantities that are needed to define a *temperature scale*, and show how these apply to the *Celsius, Kelvin,* and *Fahrenheit* temperature scales.
- Explain how a Torricellian *barometer* works.

Have you ever estimated a distance by "stepping it off"— that is, by counting the number of steps required to take you a certain distance? Or perhaps you have used the width of your hand, or the distance from your elbow to a fingertip to compare two dimensions. If so, you have engaged in what is probably the first kind of measurement ever undertaken by primitive mankind. The results of a measurement are always expressed on some kind of a *scale* that is defined in terms of a particular kind of *unit*. The first scales of distance were likely related to the human body, either directly (the length of a limb) or indirectly (the distance a man could walk in a day).

Ångstrom	1E−6 cm
Astronomical unit	1.495E8 km
Bolt (U.S., cloth)	120 ft
Cable length	720 ft
Chain (engineer's)	100 ft
Chain (surveyor's)	0.1 furlong
Cubit	18 in
Ell	45 in
Foot (U.S.)	12 in
Foot (British)	0.4 pace
Furlong	1/8 mile
Hand	4 in
Inch (U.S.)	1/12 ft
Inch (British)	1/36 yard
League	3 miles
Light year	9.46E12 km
Mile (U.S., staute)	5280 ft
Mile (nautical)	1.853 km
Nail (British)	2.25 in
Pace (British)	30 in
Parsec	3.084E13 km
Point (printer's)	1/72 in
Rope (British)	20 ft
Span	9 in

Figure 1.4.1: Current and past units of distance

Table showing various forms of units for measuring distanced used in the past and the present. Left column shows unit and right column shows value of unit measurement in terms of more commonly used units.

As civilization developed, a wide variety of measuring scales came into existence, many for the same quantity (such as length), but adapted to particular activities or trades. Eventually, it became apparent that in order for trade and commerce to be possible, these scales had to be defined in terms of standards that would allow measures to be verified, and, when expressed in different units (bushels and pecks, for example), to be correlated or converted.

History of Units

Over the centuries, hundreds of measurement units and scales have developed in the many civilizations that achieved some literate means of recording them. Some, such as those used by the Aztecs, fell out of use and were largely forgotten as these civilizations died out. Other units, such as the various systems of measurement that developed in England, achieved

prominence through extension of the Empire and widespread trade; many of these were confined to specific trades or industries. The examples shown here are only some of those that have been used to measure length or distance. The history of measuring units provides a fascinating reflection on the history of industrial development.

The most influential event in the history of measurement was undoubtedly the French Revolution and the Age of Rationality that followed. This led directly to the metric system that attempted to do away with the confusing multiplicity of measurement scales by reducing them to a few fundamental ones that could be combined in order to express any kind of quantity. The metric system spread rapidly over much of the world, and eventually even to England and the rest of the U.K. when that country established closer economic ties with Europe in the latter part of the 20th Century. The United States is presently the only major country in which "metrication" has made little progress within its own society, probably because of its relative geographical isolation and its vibrant internal economy.

Science, being a truly international endeavor, adopted metric measurement very early on; engineering and related technologies have been slower to make this change, but are gradually doing so. Even the within the metric system, however, a variety of units were employed to measure the same fundamental quantity; for example, energy could be expressed within the metric system in units of ergs, electron-volts, joules, and two kinds of calories. This led, in the mid-1960s, to the adoption of a more basic set of units, the *Systeme Internationale* (*SI*) units that are now recognized as the standard for science and, increasingly, for technology of all kinds.

The Seven *SI* Base Units and Decimal Prefixes

In principle, any physical quantity can be expressed in terms of only seven base units (Table 1.4.1), with each base unit defined by a standard described in the NIST Web site.

Table 1.4.1: The Seven Base Units

Property	Unit	Symbol
length	meter	m
mass	kilogram	kg
time	second	s
temperature (absolute)	kelvin	K
amount of substance	mole	mol
electric current	ampere	A
luminous intensity	candela	cd

A few special points about some of these units are worth noting:

- The base unit of **mass** is unique in that a decimal prefix (Table 1.4.2) is built into it; i.e., the base SI unit is not the *gram*.
- The base unit of **time** is the only one that is not metric. Numerous attempts to make it so have never garnered any success; we are still stuck with the 24:60:60 system that we inherited from ancient times. The ancient Egyptians of around 1500 BC invented the 12-hour day, and the 60:60 part is a remnant of the base-60 system that the Sumerians used for their astronomical calculations around 100 BC.
- Of special interest to Chemistry is the *mole*, the base unit for expressing the **quantity of matter**. Although the number is not explicitly mentioned in the official definition, chemists define the mole as Avogadro's number (approximately 6.02×10^{23}) of anything.

Owing to the wide range of values that quantities can have, it has long been the practice to employ prefixes such as milli and mega to indicate decimal fractions and multiples of metric units. As part of the SI standard, this system has been extended and formalized (Table 1.4.2).

Table 1.4.2: Prefixes used to scale up or down base units

Prefix	Abbreviation	Multiplier	Prefix	Abbreviation	Multiplier
peta	P	10^{15}	deci	d	10^{-1}
tera	T	10^{12}	centi	c	10^{-2}
giga	G	10^{9}	milli	m	10^{-3}
mega	M	10^{6}	micro	μ	10^{-6}
kilo	k	10^{3}	nano	n	10^{-9}
hecto	h	10^{2}	pico	p	10^{-12}
deca	da	10	femto	f	10^{-15}

Pseudo-Si Units

There is a category of units that are "honorary" members of the SI in the sense that it is acceptable to use them along with the base units defined above. These include such mundane units as the hour, minute, and degree (of angle), etc., but the three shown here are of particular interest to chemistry, and you will need to know them.

Pseudo-Si Units

liter (litre)	L	1 L = 1 dm^3 = 10^{-3} m^3
metric ton	t	1 t = 10^3 kg
united atomic mass unit (amu)	u	1 u = 1.66054×10^{-27} kg

Derived Units and Dimensions

Most of the physical quantities we actually deal with in science and also in our daily lives, have units of their own: volume, pressure, energy and electrical resistance are only a few of hundreds of possible examples. It is important to understand, however, that all of these can be expressed in terms of the SI base units; they are consequently known as *derived units*. In fact, most physical quantities can be expressed in terms of one or more of the following five fundamental units:

- mass (M)
- length (L)
- time (T)
- electric charge (Q)
- temperature (Θ theta)

Consider, for example, the unit of *volume*, which we denote as V. To measure the volume of a rectangular box, we need to multiply the lengths as measured along the three coordinates:

$$V = x \cdot y \cdot z$$

We say, therefore, that volume has the dimensions of length-cubed:

$$dim\{V\} = L^3$$

Thus the units of volume will be m^3 (in the SI) or cm^3, ft^3 (English), etc. Moreover, any formula that calculates a volume must contain within it the L^3 dimension; thus the volume of a sphere is $4/3\pi r^3$. The *dimensions* of a unit are the powers which M, L, t, Q and Q must be given in order to express the unit. Thus,

$$dim\{V\} = M^0 L^3 T^0 Q^0 \Theta^0$$

as given above.

There are several reasons why it is worthwhile to consider the dimensions of a unit.

1. Perhaps the most important use of dimensions is to help us understand the relations between various units of measure and thereby get a better understanding of their physical meaning. For example, a look at the dimensions of the frequently confused electrical terms resistance and resistivity should enable you to explain, in plain words, the difference between them.
2. By the same token, the dimensions essentially tell you how to calculate any of these quantities, using whatever specific units you wish. (Note here the distinction between dimensions and units.)
3. Just as you cannot add apples to oranges, an expression such as $a = b + cx^2$ is meaningless unless the dimensions of each side are identical. (Of course, the two sides should work out to the same units as well.)
4. Many quantities must be dimensionless— for example, the variable x in expressions such as $\log x$, e^x, and $\sin x$. Checking through the dimensions of such a quantity can help avoid errors.

The formal, detailed study of dimensions is known as *dimensional analysis* and is a topic in any basic physics course.

Example 1.4.1

Find the dimensions of energy.

Solution

When mechanical work is performed on a body, its energy increases by the amount of work done, so the two quantities are equivalent and we can concentrate on work. The latter is the product of the force applied to the object and the distance it is displaced. From Newton's law, force is the product of mass and acceleration, and the latter is the rate of change of velocity, typically expressed in meters per second per second. Combining these quantities and their dimensions yields the result shown in Table 1.4.1.

Table 1.4.3: Dimensions of units commonly used in Chemistry

Q	M	L	t	quantity	SI unit, other typical units
1	-	-	-	electric charge	coulomb
-	1	-	-	mass	kilogram, gram, metric ton, pound
-	-	1	-	length	meter, foot, mile
-	-	-	1	time	second, day, year
-	-	3	-	volume	liter, cm^3, quart, fluidounce
-	1	–3	-	density	kg m^{-3}, g cm^{-3}
-	1	1	–2	force	newton, dyne
-	1	–1	–2	pressure	pascal, atmosphere, torr
-	1	2	–2	energy	joule, erg, calorie, electron-volt
-	1	2	–3	power	watt
1	1	2	–2	electric potential	volt
1	-	-	–1	electric current	ampere
1	1	1	–2	electric field intensity	volt m^{-1}
–2	1	2	–1	electric resistance	ohm
2	1	3	–1	electric resistivity	-
2	–1	–2	1	electric conductance	siemens, mho

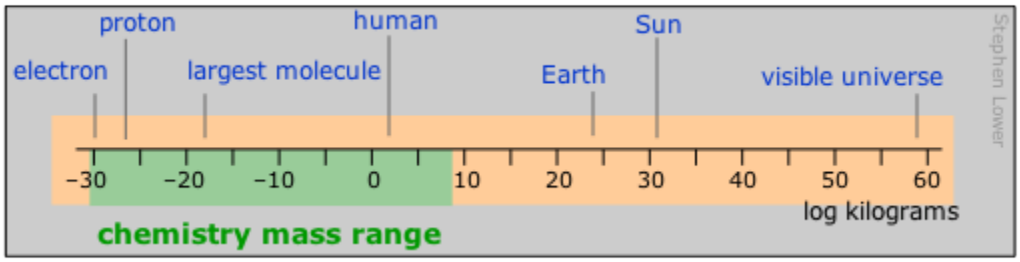
Dimensional analysis is widely employed when it is necessary to convert one kind of unit into another, and chemistry students often use it in "chemical arithmetic" calculations, in which context it is also known as the "Factor-Label" method. In this section, we will look at some of the quantities that are widely encountered in Chemistry, and at the units in which they are commonly expressed. In doing so, we will also consider the actual range of values these quantities can assume, both in nature in general, and also within the subset of nature that chemistry normally addresses. In looking over the various units of measure, it is interesting to note that their unit values are set close to those encountered in everyday human experience

Mass is not weight

These two quantities are widely confused. Although they are often used synonymously in informal speech and writing, they have different dimensions: *weight* is the *force* exerted on a mass by the local gravational field:

$$f = ma = mg \tag{1.4.1}$$

where *g* is the acceleration of gravity. While the nominal value of the latter quantity is 9.80 m s^{-2} at the Earth's surface, its exact value varies locally. Because it is a force, the SI unit of weight is properly the *newton*, but it is common practice (except in physics classes!) to use the terms "weight" and "mass" interchangeably, so the units *kilograms* and *grams* are acceptable in almost all ordinary laboratory contexts.



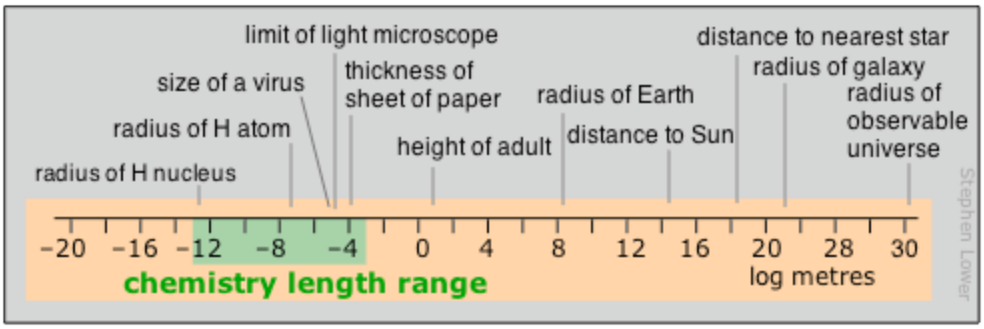
Numeric scale in terms of log kilogram. Range is negative 30 to 60 with intervals of 10. The range from negative 30 to 8 is highlighted in green to show chemistry mass range.

Please note that in this diagram and in those that follow, the numeric scale represents the *logarithm* of the number shown. For example, the mass of the electron is 10^{-30} kg.

The range of masses spans 90 orders of magnitude, more than any other unit. The range that chemistry ordinarily deals with has greatly expanded since the days when a microgram was an almost inconceivably small amount of material to handle in the laboratory; this lower limit has now fallen to the atomic level with the development of tools for directly manipulating these particles. The upper level reflects the largest masses that are handled in industrial operations, but in the recently developed fields of geochemistry and enivonmental chemistry, the range can be extended indefinitely. Flows of elements between the various regions of the environment (atmosphere to oceans, for example) are often quoted in teragrams.

Length

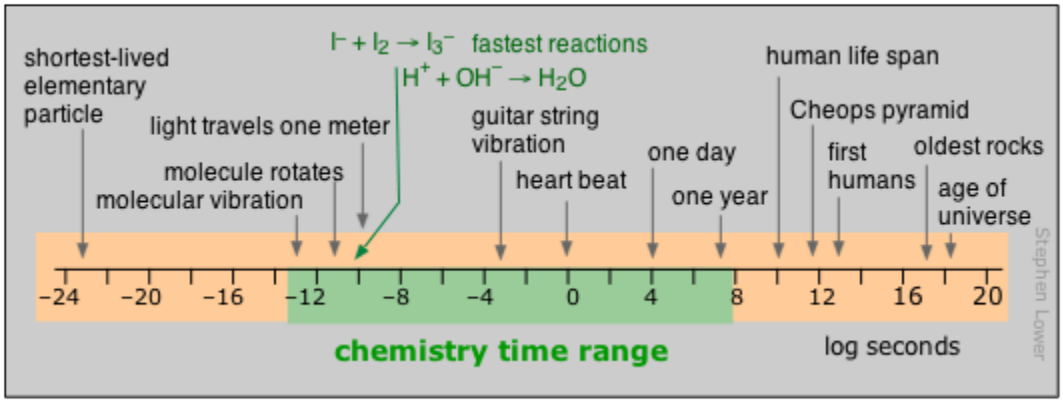
Chemists tend to work mostly in the moderately-small part of the distance range. Those who live in the lilliputian world of crystal- and molecular structures and atomic radii find the *picometer* a convenient currency, but one still sees the older non-SI unit called the *Ångstrom* used in this context; 1Å = 10^{-10} m = 100pm. Nanotechnology, the rage of the present era, also resides in this realm. The largest polymeric molecules and colloids define the top end of the particulate range; beyond that, in the normal world of doing things in the lab, the *centimeter* and occasionally the *millimeter* commonly rule.



Numeric scale in terms of log meters. Range is negative 20 to 30 with intervals of 4. The range from negative 12 to negative 4 is highlighted in green to show chemistry length range.

Time

For humans, time moves by the heartbeat; beyond that, it is the motions of our planet that count out the hours, days, and years that eventually define our lifetimes. Beyond the few thousands of years of history behind us, those years-to-the-powers-of-tens that are the fare for such fields as evolutionary biology, geology, and cosmology, cease to convey any real meaning for us. Perhaps this is why so many people are not very inclined to accept their validity.

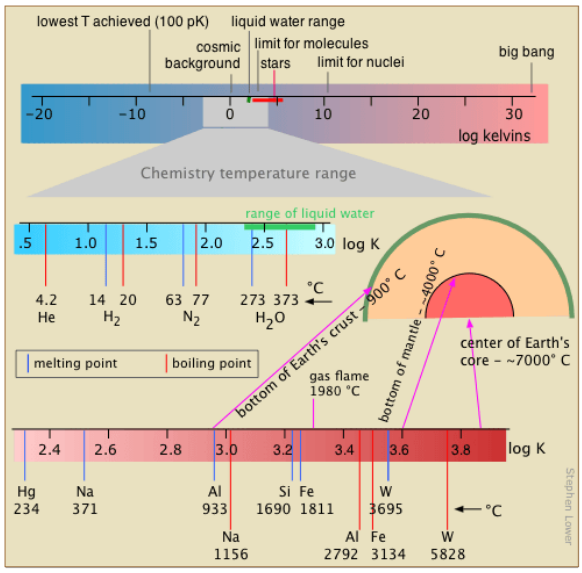


Numeric scale in terms of log seconds. Range is negative 24 to 20 with intervals of 4. The range from negative 12 to 8 is highlighted in green to show chemistry time range.

Most of what actually takes place in the chemist's test tube operates on a far shorter time scale, although there is no limit to how slow a reaction can be; the upper limits of those we can directly study in the lab are in part determined by how long a graduate student can wait around before moving on to gainful employment. Looking at the microscopic world of atoms and molecules themselves, the time scale again shifts us into an unreal world where numbers tend to lose their meaning. You can gain some appreciation of the duration of a nanosecond by noting that this is about how long it takes a beam of light to travel between your two outstretched hands. In a sense, the material foundations of chemistry itself are defined by time: neither a new element nor a molecule can be recognized as such unless it lasts long enough to have its "picture" taken through measurement of its distinguishing properties.

Temperature

Temperature, the measure of thermal intensity, spans the narrowest range of any of the base units of the chemist's measurement toolbox. The reason for this is tied into temperature's meaning as a measure of the intensity of thermal kinetic energy. Chemical change occurs when atoms are jostled into new arrangements, and the weakness of these motions brings most chemistry to a halt as absolute zero is approached. At the upper end of the scale, thermal motions become sufficiently vigorous to shake molecules into atoms, and eventually, as in stars, strip off the electrons, leaving an essentially reaction-less gaseous fluid, or plasma, of bare nuclei (ions) and electrons.



Numeric scale in terms of log Kelvins. Range is negative 20 to 30 with intervals of 10. The range from negative 3 to 4 is highlighted to show chemistry temperature range. This range is magnified further to show two numeric scales, one highlighting the lower range and the other the upper range. Melting and boiling points of different compounds are also shown in the scale.

The degree is really an *increment* of temperature, a fixed fraction of the distance between two defined reference points on a *temperature scale*.

> Although rough means of estimating and comparing temperatures have been around since AD 170, the first mercury thermometer and temperature scale were introduced in Holland in 1714 by Gabriel Daniel Fahrenheit. Fahrenheit established three fixed points on his thermometer. Zero degrees was the temperature of an ice, water, and salt mixture, which was about the coldest temperature that could be reproduced in a laboratory of the time. When he omitted salt from the slurry, he reached his second fixed point when the water-ice combination stabilized at "the thirty-second degree." His third fixed point was "found at the ninety-sixth degree, and the spirit expands to this degree when the thermometer is held in the mouth or under the armpit of a living man in good health."
>
> After Fahrenheit died in 1736, his thermometer was recalibrated using 212 degrees, the temperature at which water boils, as the upper fixed point. Normal human body temperature registered 98.6 rather than 96. In 1743, the Swedish astronomer Anders Celsius devised the aptly-named *centigrade* scale that places exactly 100 degrees between the two reference points defined by the freezing and boiling points of water.

When we say that the temperature is so many degrees, we must specify the particular scale on which we are expressing that temperature. A temperature scale has two defining characteristics, both of which can be chosen arbitrarily:

- The temperature that corresponds to 0° on the scale;
- The magnitude of the *unit increment* of temperature– that is, the size of the *degree*.

To express a temperature given on one scale in terms of another, it is necessary to take both of these factors into account. The key to temperature conversions is easy if you bear in mind that between the so-called ice- and steam-points of water there are 180 Fahrenheit degrees, but only 100 Celsius degrees, making the F° 100/180 = 5/9 the magnitude of the C°. Note the distinction between "°C" (a *temperature*) and "C°" (a temperature *increment*). Because the ice point is at 32°F, the two scales are offset by this amount. If you remember this, there is no need to memorize a conversion formula; you can work it out whenever you need it.

Near the end of the 19th Century when the physical significance of temperature began to be understood, the need was felt for a temperature scale whose zero really means zero— that is, the complete absence of thermal motion. This gave rise to the *absolute temperature scale* whose zero point is –273.15 °C, but which retains the same degree magnitude as the Celsius scale. This eventually got renamed after Lord Kelvin (William Thompson); thus the Celsius degree became the *kelvin*. Thus we can now

express an increment such as five C° as “five kelvins”

The "other" Absolute Scale

In 1859 the Scottish engineer and physicist William J. M. Rankine proposed an absolute temperature scale based on the Fahrenheit degree. Absolute zero (0° Ra) corresponds to −459.67°F. The Rankine scale has been used extensively by those same American and English engineers who delight in expressing heat capacities in units of BTUs per pound per F°.

The importance of absolute temperature scales is that absolute temperatures can be entered directly in all the fundamental formulas of physics and chemistry in which temperature is a variable.

YouTube Video

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Units of Temperature: Units of Temperature, YouTube(opens in new window) [youtu.be] (opens in new window)

Pressure

Pressure is the measure of the *force* exerted on a unit area of surface. Its SI units are therefore newtons per square meter, but we make such frequent use of pressure that a derived SI unit, the *pascal*, is commonly used:

$$1\ Pa = 1\ N\ m^{-2}$$

The concept of pressure first developed in connection with studies relating to the atmosphere and vacuum that were carried out in the 17th century.

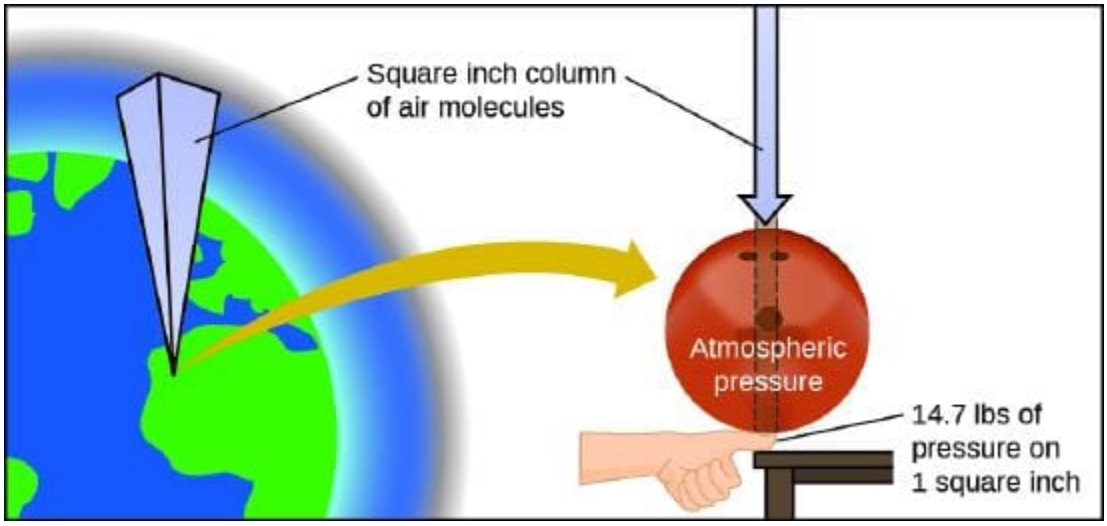


Figure 1.4.1: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

Diagram of Earth with a square inch column of air molecules extending to the atmosphere. This column points to an arrow pointing down on a bowling ball resting on a human thumbnail placed on top of a table.

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the

tanker car below. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is twice the usual pressure, and the sensation is unpleasant.

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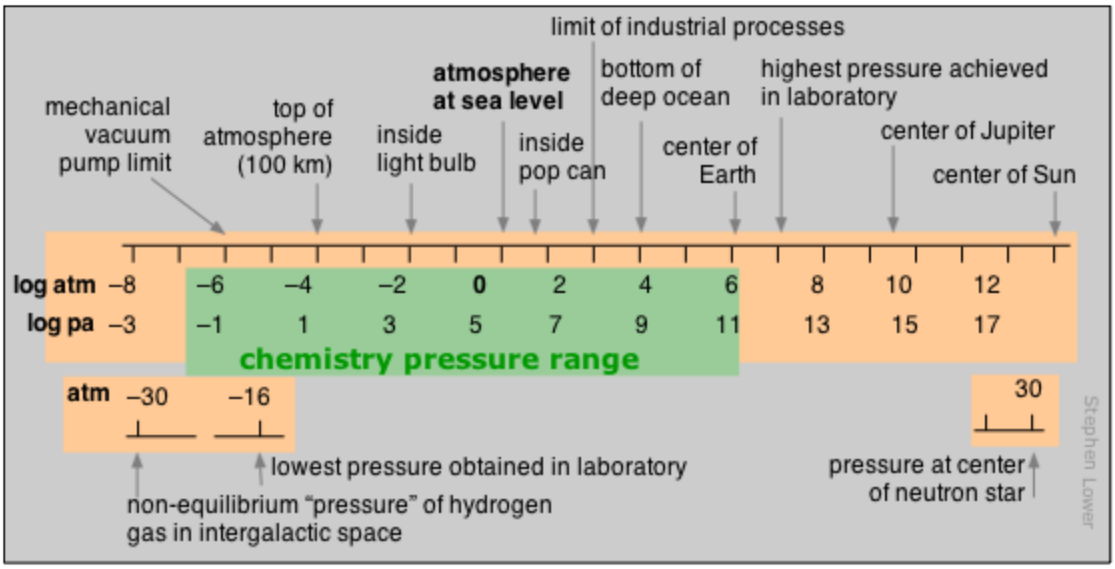
Video 1.4.1: A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased. A smaller scale demonstration of this phenomenon is briefly explained.

The molecules of a gas are in a state of constant thermal motion, moving in straight lines until experiencing a collision that exchanges momentum between pairs of molecules and sends them bouncing off in other directions. This leads to a completely random distribution of the molecular velocities both in speed and direction— or it would in the absence of the Earth's gravitational field which exerts a tiny downward force on each molecule, giving motions in that direction a very slight advantage. In an ordinary container this effect is too small to be noticeable, but in a very tall column of air the effect adds up: the molecules in each vertical layer experience more downward-directed hits from those above it. The resulting force is quickly randomized, resulting in an increased pressure in that layer which is then propagated downward into the layers below.

At sea level, the total mass of the sea of air pressing down on each 1-cm^2 of surface is about 1034 g, or 10340 kg m^{-2}. The force (weight) that the Earth's gravitional acceleration g exerts on this mass is

$$f = ma = mg = (10340\ kg)(9.81\ m\ s^{-2}) = 1.013 \times 10^5\ kg\ m\ s^{-2} = 1.013 \times 10^5\ N$$

resulting in a pressure of 1.013 × 10^5 n m^{-2} = 1.013 × 10^5 Pa. The actual pressure at sea level varies with atmospheric conditions, so it is customary to define standard atmospheric pressure as 1 atm = 1.01325 x 10^5 Pa or 101.325 kPa. Although the standard atmosphere is not an SI unit, it is still widely employed. In meteorology, the *bar*, exactly 1.000 × 10^5 = 0.967 atm, is often used.



Numeric scale given in terms of log atm and log pascals respectively. Range is negative 8 to 12 with intervals of 2 atm and negative 3 to 17 with intervals of 2 pascals. The range from negative 6 to 6 atm and negative 1 to 11 pascals is highlighted to show chemistry pressure range.

The Barometer

In the early 17th century, the Italian physicist and mathematician Evangalisto Torricelli invented a device to measure atmospheric pressure. The Torricellian *barometer* consists of a vertical glass tube closed at the top and open at the bottom. It is filled with a liquid, traditionally mercury, and is then inverted, with its open end immersed in the container of the same liquid. The liquid level in the tube will fall under its own weight until the downward force is balanced by the vertical force transmitted hydrostatically to the column by the downward force of the atmosphere acting on the liquid surface in the open container. Torricelli was also the first to recognize that the space above the mercury constituted a vacuum, and is credited with being the first to create a vacuum.

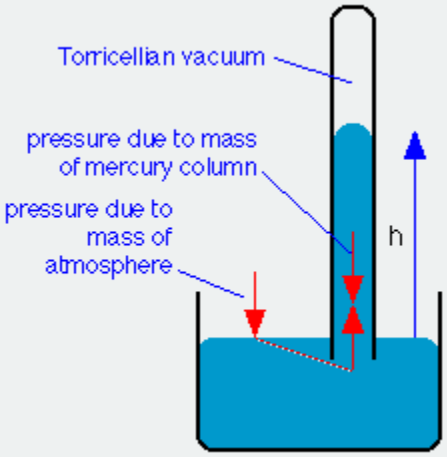


Diagram showing a barometer setup with arrows pointing on the surface of the liquid to indicate pressure due to atmosphere as well as arrow pointing up in the vertical tube to show height of liquid in the tube.

One *standard atmosphere* will support a column of mercury that is 760 mm high, so the "millimeter of mercury", now more commonly known as the *torr*, has long been a common pressure unit in the sciences: 1 atm = 760 torr.

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International System of Units (SI Units): International System of Units (SI Units), YouTube(opens in new window) [youtu.be]

Summary

The natural sciences begin with ***observation*****,** and this usually involves ***numerical measurements*** of quantities such as length, volume, density, and temperature. Most of these quantities have ***units*** of some kind associated with them, and these units must be retained when you use them in calculations. Measuring units can be defined in terms of a very small number of fundamental ones that, through "dimensional analysis", provide insight into their derivation and meaning, and must be understood when converting between different unit systems.

Contributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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1.5: Uncertainty in Measurement

Learning Objectives

- To introduce the fundamental mathematical skills you will need to complete basic chemistry questions and problems

Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal of scientists is to obtain measured values that are both accurate and precise.

Suppose, for example, that the mass of a sample of gold was measured on one balance and found to be 1.896 g. On a different balance, the same sample was found to have a mass of 1.125 g. Which was correct? Careful and repeated measurements, including measurements on a calibrated third balance, showed the sample to have a mass of 1.895 g. The masses obtained from the three balances are in the following table:

Masses Obtained from the three balances

Balance 1	Balance 2	Balance 3
1.896 g	1.125 g	1.893 g
1.895 g	1.158 g	1.895 g
1.894 g	1.067 g	1.895 g

Whereas the measurements obtained from balances 1 and 3 are reproducible (precise) and are close to the accepted value (accurate), those obtained from balance 2 are neither. Even if the measurements obtained from balance 2 had been precise (if, for example, they had been 1.125, 1.124, and 1.125), they still would not have been accurate. We can assess the precision of a set of measurements by calculating the average deviation of the measurements as follows:

1. Calculate the average value of all the measurements:

$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}} \tag{1.5.1}$$

2. Calculate the deviation of each measurement, which is the absolute value of the difference between each measurement and the average value:

$$\text{deviation} = |\text{measurement} - \text{average}| \tag{1.5.2}$$

where $|\ |$ means absolute value (i.e., convert any negative number to a positive number).

3. Add all the deviations and divide by the number of measurements to obtain the average deviation:

$$\text{average} = \frac{\text{sum of deviations}}{\text{number of measurements}} \tag{1.5.3}$$

Then we can express the precision as a percentage by dividing the average deviation by the average value of the measurements and multiplying the result by 100. In the case of balance 2, the average value is

$$\frac{1.125\ g + 1.158\ g + 1.067\ g}{3} = 1.117\ g$$

The deviations are

- $|1.125\ \ g - 1.117\ \ g| = 0.008\ \ g$
- $|1.158\ \ g - 1.117\ \ g| = 0.041\ \ g$, and
- $|1.067\ \ g - 1.117\ \ g| = 0.050\ \ g$.

So the average deviation is

$$\frac{0.008\ g + 0.041\ g + 0.050\ g}{3} = 0.033\ g$$

The precision of this set of measurements is therefore

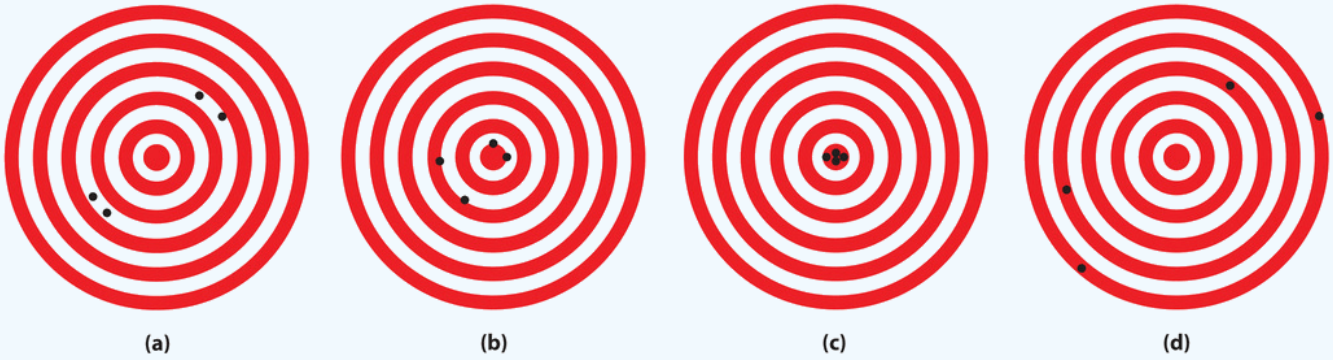
$$\frac{0.033\ g}{1.117\ g} \times 100 = 3.0\%$$

When a series of measurements is precise but not accurate, the error is usually systematic. Systematic errors can be caused by faulty instrumentation or faulty technique.

Example 1.5.1

The following archery targets show marks that represent the results of four sets of measurements. Which target shows

a. a precise but inaccurate set of measurements?
b. an accurate but imprecise set of measurements?
c. a set of measurements that is both precise and accurate?
d. a set of measurements that is neither precise nor accurate?



Example 1.5.2

a. A 1-carat diamond has a mass of 200.0 mg. When a jeweler repeatedly weighed a 2-carat diamond, he obtained measurements of 450.0 mg, 459.0 mg, and 463.0 mg. Were the jeweler's measurements accurate? Were they precise?
b. A single copper penny was tested three times to determine its composition. The first analysis gave a composition of 93.2% zinc and 2.8% copper, the second gave 92.9% zinc and 3.1% copper, and the third gave 93.5% zinc and 2.5% copper. The actual composition of the penny was 97.6% zinc and 2.4% copper. Were the results accurate? Were they precise?

Solution

a. The expected mass of a 2-carat diamond is 2 × 200.0 mg = 400.0 mg. The average of the three measurements is 457.3 mg, about 13% greater than the true mass. These measurements are not particularly accurate.

The deviations of the measurements are 7.3 mg, 1.7 mg, and 5.7 mg, respectively, which give an average deviation of 4.9 mg and a precision of

$$\frac{4.9mg}{457.3mg} \times 100 = 1.1\%$$

These measurements are rather *precise*.

b. The average values of the measurements are 93.2% zinc and 2.8% copper versus the true values of 97.6% zinc and 2.4% copper. Thus these measurements are not very accurate, with errors of −4.5% and + 17% for zinc and copper, respectively. (The sum of the measured zinc and copper contents is only 96.0% rather than 100%, which tells us that either there is a significant error in one or both measurements or some other element is present.)

The deviations of the measurements are 0.0%, 0.3%, and 0.3% for both zinc and copper, which give an average deviation of 0.2% for both metals. We might therefore conclude that the measurements are equally precise, but that is not the case. Recall that precision is the average deviation divided by the average value times 100. Because the average value of the zinc measurements is much greater than the average value of the copper measurements (93.2% versus 2.8%), the copper measurements are much less precise.

$$\text{precision (Zn)} = \frac{0.2\%}{93.2\%} \times 100 = 0.2\%$$

$$\text{precision (Cu)} = \frac{0.2\%}{2.8\%} \times 100 = 7\%$$

Significant Figures

No measurement is free from error. Error is introduced by the limitations of instruments and measuring devices (such as the size of the divisions on a graduated cylinder) and the imperfection of human senses (i.e., detection). Although errors in calculations can be enormous, they do not contribute to uncertainty in measurements. Chemists describe the estimated degree of error in a measurement as the uncertainty of the measurement, and they are careful to report all measured values using only significant figures, numbers that describe the value without exaggerating the degree to which it is known to be accurate. Chemists report as significant all numbers known with absolute certainty, plus one more digit that is understood to contain some uncertainty. The uncertainty in the final digit is usually assumed to be ±1, unless otherwise stated.

Significant Figure Rules

The following rules have been developed for counting the number of significant figures in a measurement or calculation:

1. Any nonzero digit is significant.
2. Any zeros between nonzero digits are significant. The number 2005, for example, has four significant figures.
3. Any zeros used as a placeholder preceding the first nonzero digit are not significant. So 0.05 has one significant figure because the zeros are used to indicate the placement of the digit 5. In contrast, 0.050 has two significant figures because the last two digits correspond to the number 50; the last zero is not a placeholder. As an additional example, 5.0 has two significant figures because the zero is used not to place the 5 but to indicate 5.0.
4. When a number does not contain a decimal point, zeros added after a nonzero number may or may not be significant. An example is the number 100, which may be interpreted as having one, two, or three significant figures. (Note: treat all trailing zeros in exercises and problems in this text as significant unless you are specifically told otherwise.)
5. Integers obtained either by counting objects or from definitions are exact numbers, which are considered to have infinitely many significant figures. If we have counted four objects, for example, then the number 4 has an infinite number of significant figures (i.e., it represents 4.000...). Similarly, 1 foot (ft) is defined to contain 12 inches (in), so the number 12 in the following equation has infinitely many significant figures:

$$1\,\text{ft} = 1,\text{in}$$

An effective method for determining the number of significant figures is to convert the measured or calculated value to scientific notation because any zero used as a placeholder is eliminated in the conversion. When 0.0800 is expressed in scientific notation as 8.00×10^{-2}, it is more readily apparent that the number has three significant figures rather than five; in scientific notation, the number preceding the exponential (i.e., N) determines the number of significant figures.

Example 1.5.3

Give the number of significant figures in each. Identify the rule for each.

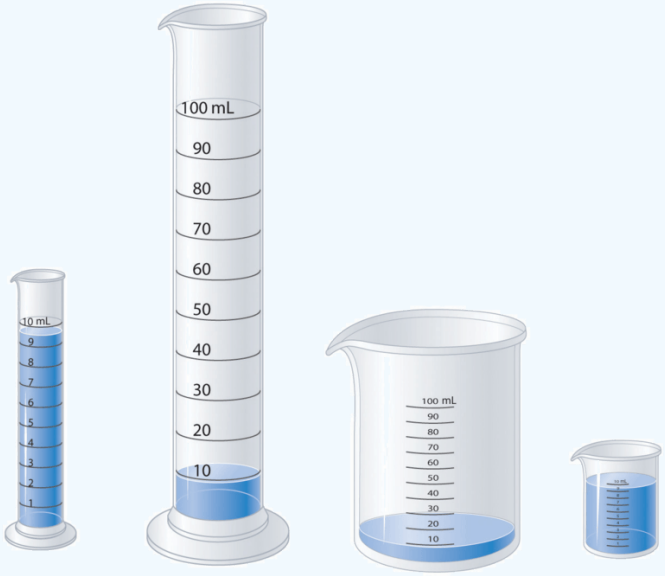
a. 5.87
b. 0.031
c. 52.90
d. 00.2001
e. 500
f. 6 atoms

Solution

a. three (rule 1)
b. two (rule 3); in scientific notation, this number is represented as 3.1×10^{-2}, showing that it has two significant figures.
c. four (rule 3)
d. four (rule 2); this number is 2.001×10^{-1} in scientific notation, showing that it has four significant figures.
e. one, two, or three (rule 4)
f. infinite (rule 5)

Example 1.5.4

Which measuring apparatus would you use to deliver 9.7 mL of water as accurately as possible? To how many significant figures can you measure that volume of water with the apparatus you selected?



Answer available at the end of this section.

Mathematical operations are carried out using all the digits given and then rounding the final result to the correct number of significant figures to obtain a reasonable answer. This method avoids compounding inaccuracies by successively rounding intermediate calculations. After you complete a calculation, you may have to round the last significant figure up or down depending on the value of the digit that follows it. If the digit is 5 or greater, then the number is rounded up. For example, when rounded to three significant figures, 5.215 is 5.22, whereas 5.213 is 5.21. Similarly, to three significant figures, 5.005 kg becomes 5.01 kg, whereas 5.004 kg becomes 5.00 kg. The procedures for dealing with significant figures are different for addition and subtraction versus multiplication and division.

When we add or subtract measured values, the value with the fewest significant figures to the right of the decimal point determines the number of significant figures to the right of the decimal point in the answer. Drawing a vertical line to the right of the column corresponding to the smallest number of significant figures is a simple method of determining the proper number of significant figures for the answer:

$$3240.7 + 21.236 = 3261.9|36$$

The line indicates that the digits 3 and 6 are not significant in the answer. These digits are not significant because the values for the corresponding places in the other measurement are unknown (3240.7??). Consequently, the answer is expressed as 3261.9, with five significant figures. Again, numbers greater than or equal to 5 are rounded up. If our second number in the calculation had been 21.256, then we would have rounded 3261.956 to 3262.0 to complete our calculation.

When we multiply or divide measured values, the answer is limited to the smallest number of significant figures in the calculation; thus,

$$42.9 \times 8.323 = 357.057 = 357.$$

Although the second number in the calculation has four significant figures, we are justified in reporting the answer to only three significant figures because the first number in the calculation has only three significant figures. An exception to this rule occurs when multiplying a number by an integer, as in 12.793 × 12. In this case, the number of significant figures in the answer is determined by the number 12.973, because we are in essence adding 12.973 to itself 12 times. The correct answer is therefore 155.516, an increase of one significant figure, not 155.52.

When you use a calculator, it is important to remember that the number shown in the calculator display often shows more digits than can be reported as significant in your answer. When a measurement reported as 5.0 kg is divided by 3.0 L, for example, the display may show 1.666666667 as the answer. We are justified in reporting the answer to only two significant figures, giving 1.7 kg/L as the answer, with the last digit understood to have some uncertainty.

In calculations involving several steps, slightly different answers can be obtained depending on how rounding is handled, specifically whether rounding is performed on intermediate results or postponed until the last step. Rounding to the correct number of significant figures should always be performed at the end of a series of calculations because rounding of intermediate results can sometimes cause the final answer to be significantly in error.

Example 1.5.5

Complete the calculations and report your answers using the correct number of significant figures.

a. 87.25 mL + 3.0201 mL
b. 26.843 g + 12.23 g
c. 6 × 12.011
d. 2(1.008) g + 15.99 g
e. 137.3 + 2(35.45)
f. $\frac{118.7}{2}g - 35.5g$
g. $47.23g - \frac{207.2}{5.92}g$
h. $\frac{77.604}{6.467} - 4.8$
i. $\frac{24.86}{2.0} - 3.26(0.98)$
j. $(15.9994 \times 9) + 2.0158$

Solution

a. 90.27 mL
b. 39.07 g
c. 72.066 (See rule 5 under “Significant Figures.”)
d. 2(1.008) g + 15.99 g = 2.016 g + 15.99 g = 18.01 g
e. 137.3 + 2(35.45) = 137.3 + 70.90 = 208.2
f. 59.35 g – 35.5 g = 23.9 g
g. 47.23 g – 35.0 g = 12.2 g
h. 12.00 – 4.8 = 7.2
i. 12 – 3.2 = 9
j. 143.9946 + 2.0158 = 146.0104

In practice, chemists generally work with a calculator and carry all digits forward through subsequent calculations. When working on paper, however, we often want to minimize the number of digits we have to write out. Because successive rounding

can compound inaccuracies, intermediate roundings need to be handled correctly. When working on paper, always round an intermediate result so as to retain at least one more digit than can be justified and carry this number into the next step in the calculation. The final answer is then rounded to the correct number of significant figures at the very end.

In the worked examples in this text, we will often show the results of intermediate steps in a calculation. In doing so, we will show the results to only the correct number of significant figures allowed for that step, in effect treating each step as a separate calculation. This procedure is intended to reinforce the rules for determining the number of significant figures, but in some cases it may give a final answer that differs in the last digit from that obtained using a calculator, where all digits are carried through to the last step.

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Significant Figures: Significant Figures, YouTube(opens in new window) [youtu.be]

Answers

Example 1.5.4

Use the 10 mL graduated cylinder, which will be accurate to two significant figures.

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1.6: Dimensional Analysis

Learning Objectives

- To be introduced to the dimensional analysis and how it can be used to aid basic chemistry problem solving.
- To use dimensional analysis to identify whether an equation is set up correctly in a numerical calculation
- To use dimensional analysis to facilitate the conversion of units.

Dimensional analysis is amongst the most valuable tools physical scientists use. Simply put, it is the conversion between an amount in one unit to the corresponding amount in a desired unit using various conversion factors. This is valuable because certain measurements are more accurate or easier to find than others.

A Macroscopic Example: Party Planning

If you have every planned a party, you have used dimensional analysis. The amount of beer and munchies you will need depends on the number of people you expect. For example, if you are planning a Friday night party and expect 30 people you might estimate you need to go out and buy 120 bottles of sodas and 10 large pizza's. How did you arrive at these numbers? The following indicates the type of dimensional analysis solution to party problem:

$$(30\ \cancel{humans}\ ) \times \left(\frac{4 \text{ sodas}}{1\ \cancel{human}} \right) = 120 \text{ sodas} \tag{1.6.1}$$

$$(30\ \cancel{humans}\ ) \times \left(\frac{0.333 \text{ pizzas}}{1\ \cancel{human}} \right) = 10 \text{ pizzas} \tag{1.6.2}$$

Notice that the units that canceled out are lined out and only the desired units are left (discussed more below). Finally, in going to buy the soda, you perform another dimensional analysis: should you buy the sodas in six-packs or in cases?

$$(120\ sodas) \times \left(\frac{1 \text{ six pack}}{6\ sodas} \right) = 20 \text{ six packs} \tag{1.6.3}$$

$$(120\ sodas) \times \left(\frac{1 \text{ case}}{24\ sodas} \right) = 5 \text{ cases} \tag{1.6.4}$$

Realizing that carrying around 20 six packs is a real headache, you get 5 cases of soda instead.

In this party problem, we have used dimensional analysis in two different ways:

- In the first application (Equations 1.6.1 and Equation 1.6.2), dimensional analysis was used to calculate how much soda is needed need. This is based on knowing: (1) how much soda we need for one person and (2) how many people we expect; likewise for the pizza.
- In the second application (Equations 1.6.3 and 1.6.4), dimensional analysis was used to ***convert units*** (i.e. from individual sodas to the equivalent amount of six packs or cases)

Using Dimensional Analysis to Convert Units

Consider the conversion in Equation 1.6.3:

$$(120\ sodas) \times \left(\frac{1 \text{ six pack}}{6\ sodas} \right) = 20 \text{ six packs} \tag{1.6.5}$$

If we ignore the numbers for a moment, and just look at the units (i.e. ***dimensions***), we have:

$$\text{soda} \times \left(\frac{\text{six pack}}{\text{sodas}} \right)$$

We can treat the dimensions in a similar fashion as other numerical analyses (i.e. any number divided by itself is 1). Therefore:

$$\text{soda} \times \left(\frac{\text{six pack}}{\text{sodas}} \right) = \cancel{\text{soda}} \times \left(\frac{\text{six pack}}{\cancel{\text{sodas}}} \right)$$

So, the dimensions of the numerical answer will be "six packs".

How can we use dimensional analysis to be sure we have set up our equation correctly? Consider the following alternative way to set up the above unit conversion analysis:

$$120 \cancel{\text{soda}} \times \left(\frac{6 \text{ sodas}}{\cancel{\text{six pack}}} \right) = 720 \frac{\text{sodas}^2}{1 \text{ six pack}}$$

- While it is correct that there are 6 sodas in one six pack, the above equation yields a value of 720 with units of ***sodas^2/six pack***.
- These rather bizarre units indicate that the equation has been setup ***incorrectly*** (and as a consequence you will have a ton of extra soda at the party).

Using Dimensional Analysis in Calculations

In the above case it was relatively straightforward keeping track of units during the calculation. What if the calculation involves powers, etc? For example, the equation relating kinetic energy to mass and velocity is:

$$E_{kinetics} = \frac{1}{2} \text{mass} \times \text{velocity}^2 \tag{1.6.6}$$

An example of units of mass is kilograms (kg) and velocity might be in meters/second (m/s). What are the dimensions of $E_{kinetic}$?

$$(kg) \times \left(\frac{m}{s} \right)^2 = \frac{kg\, m^2}{s^2}$$

The $\frac{1}{2}$ factor in Equation 1.6.6 is neglected since pure numbers have no units. Since the velocity is squared in Equation 1.6.6, the ***dimensions*** associated with the numerical value of the velocity are also squared. We can double check this by knowing the the Joule (J) is a measure of energy, and as a composite unit can be decomposed thusly:

$$1\ J = kg \frac{m^2}{s^2}$$

Units of Pressure

Pressure (*P*) is a measure of the Force (*F*) per unit area (*A*):

$$P = \frac{F}{A}$$

Force, in turn, is a measure of the acceleration (a) on a mass (m):

$$F = m \times a$$

Thus, pressure (P) can be written as:

$$P = \frac{m \times a}{A}$$

What are the units of pressure from this relationship? (*Note: acceleration is the change in velocity per unit time*)

$$P = \frac{kg \times \frac{\cancel{m}}{s^2}}{m^{\cancel{2}}}$$

We can simplify this description of the units of Pressure by dividing numerator and denominator by m:

$$P = \frac{\frac{kg}{s^2}}{m} = \frac{kg}{m\ s^2}$$

In fact, these are the units of a the composite *Pascal* (*Pa*) unit and is the SI measure of pressure.

Performing Dimensional Analysis

The use of units in a calculation to ensure that we obtain the final proper units is called *dimensional analysis*. For example, if we observe experimentally that an object's potential energy is related to its mass, its height from the ground, and to a gravitational force, then when multiplied, the units of mass, height, and the force of gravity must give us units corresponding to those of energy.

Energy is typically measured in joules, calories, or electron volts (eV), defined by the following expressions:

- 1 J = 1 (kg·m^2)/s^2 = 1 coulomb·volt
- 1 cal = 4.184 J
- 1 eV = 1.602 × 10^{-19} J

Performing dimensional analysis begins with finding the appropriate conversion factors. Then, you simply multiply the values together such that the units cancel by having equal units in the numerator and the denominator. To understand this process, let us walk through a few examples.

Example 1.6.1

Imagine that a chemist wants to measure out 0.214 mL of benzene, but lacks the equipment to accurately measure such a small volume. The chemist, however, is equipped with an analytical balance capable of measuring to $\pm 0.0001\ \ g$. Looking in a reference table, the chemist learns the density of benzene ($\rho = 0.8765\ \ g/mL$). How many grams of benzene should the chemist use?

Solution

$$0.214\ \cancel{mL}\left(\frac{0.8765\ g}{1\ \cancel{mL}}\right) = 0.187571\ g$$

Notice that the mL are being divided by mL, an equivalent unit. We can cancel these our, which results with the 0.187571 g. However, this is not our final answer, since this result has too many significant figures and must be rounded down to three significant digits. This is because 0.214 mL has three significant digits and the conversion factor had four significant digits. Since 5 is greater than or equal to 5, we must round the preceding 7 up to 8.

Hence, the chemist should weigh out 0.188 g of benzene to have 0.214 mL of benzene.

Example 1.6.2

To illustrate the use of dimensional analysis to solve energy problems, let us calculate the kinetic energy in joules of a 320 g object traveling at 123 cm/s.

Solution

To obtain an answer in joules, we must convert grams to kilograms and centimeters to meters. Using Equation 1.6.6, the calculation may be set up as follows:

\[\begin{align*} KE&=\dfrac{1}{2}mv^2=\dfrac{1}{2}(g) \left(\dfrac{kg}{g}\right) \left[\left(\dfrac{cm}{s}\right)\left(\dfrac{m}{cm}\right) \right]^2 \[4pt] &= (\cancel{g})\left(\dfrac{kg}{\cancel{g}}\right) \left(\dfrac{\cancel{m^2}}{s^2}\right) \left(\dfrac{m^2}{\cancel{cm^2}}\right) = \dfrac{kg \cdot m^2}{s^2} \[4pt] &=\dfrac{1}{2}320\; \cancel{g} \left(\dfrac{1\; kg}{1000\;\cancel{g}}\right) \left[\left(\dfrac{123\;\cancel{cm}}{1 \;s}\right) \left(\dfrac{1 \;m}{100\; \cancel{cm}}\right) \right]^2=\dfrac{0.320\; kg}{2}\left[\dfrac{123 m}{s(100)}\right]^2 \[4pt] &=\dfrac{1}{2} 0.320\; kg \left[\dfrac{(123)^2 m^2}{s^2(100)^2} \right]= 0.242 \dfrac{kg \cdot m^2}{s^2} = 0.242\; J \end{align*} \nonumber \]

Alternatively, the conversions may be carried out in a stepwise manner:

Step 1: convert g to kg

$$320 \; \cancel{g} \left(\frac{1 \; kg}{1000 \; \cancel{g}} \right) = 0.320 \; kg$$

Step 2: convert cm to m

$$123 \; \cancel{cm} \left(\frac{1 \; m}{100 \; \cancel{cm}} \right) = 1.23 \; m$$

Now the natural units for calculating joules is used to get final results

$$\begin{aligned} KE &= \frac{1}{2} 0.320 \; kg \, (1.23 \; ms)^2 \\ &= \frac{1}{2} 0.320 \; kg \left(1.513 \frac{m^2}{s^2} \right) = 0.242 \; \frac{kg \cdot m^2}{s^2} = 0.242 \; J \end{aligned}$$

Of course, steps 1 and 2 can be done in the opposite order with no effect on the final results. However, this second method involves an additional step.

Example 1.6.3

Now suppose you wish to report the number of kilocalories of energy contained in a 7.00 oz piece of chocolate in units of kilojoules per gram.

Solution

To obtain an answer in kilojoules, we must convert 7.00 oz to grams and kilocalories to kilojoules. Food reported to contain a value in Calories actually contains that same value in kilocalories. If the chocolate wrapper lists the caloric content as 120 Calories, the chocolate contains 120 kcal of energy. If we choose to use multiple steps to obtain our answer, we can begin with the conversion of kilocalories to kilojoules:

$$120 \; \cancel{kcal} \left(\frac{1000 \; \cancel{cal}}{\cancel{kcal}} \right) \left(\frac{4.184 \; \cancel{J}}{1 \; \cancel{cal}} \right) \left(\frac{1 \; kJ}{1000 \; \cancel{J}} \right) = 502 \; kJ$$

We next convert the 7.00 oz of chocolate to grams:

$$7.00 \; \cancel{oz} \left(\frac{28.35 \; g}{1 \; \cancel{oz}} \right) = 199 \; g$$

The number of kilojoules per gram is therefore

$$\frac{502 \; kJ}{199 \; g} = 2.52 \; kJ/g$$

Alternatively, we could solve the problem in one step with all the conversions included:

$$\left(\frac{120\ \cancel{kcal}}{7.00\ \cancel{oz}}\right)\left(\frac{1000\ \cancel{cal}}{1\ \cancel{kcal}}\right)\left(\frac{4.184\ \cancel{J}}{1\ \cancel{cal}}\right)\left(\frac{1\ kJ}{1000\ \cancel{J}}\right)\left(\frac{1\ \cancel{oz}}{28.35\ g}\right) = 2.53\ kJ/g$$

The discrepancy between the two answers is attributable to rounding to the correct number of significant figures for each step when carrying out the calculation in a stepwise manner. Recall that all digits in the calculator should be carried forward when carrying out a calculation using multiple steps. In this problem, we first converted kilocalories to kilojoules and then converted ounces to grams.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Converting Between Units: Converting Between Units, YouTube(opens in new window) [youtu.be]

Summary

Dimensional analysis is used in numerical calculations, and in converting units. It can help us identify whether an equation is set up correctly (i.e. the resulting units should be as expected). Units are treated similarly to the associated numerical values, i.e., if a variable in an equation is supposed to be squared, then the associated dimensions are squared, etc.

Contributors and Attributions

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1.E: Matter and Measurement (Exercises)

These are homework exercises to accompany the Textmap created for "Chemistry: The Central Science" by Brown et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.

1.2

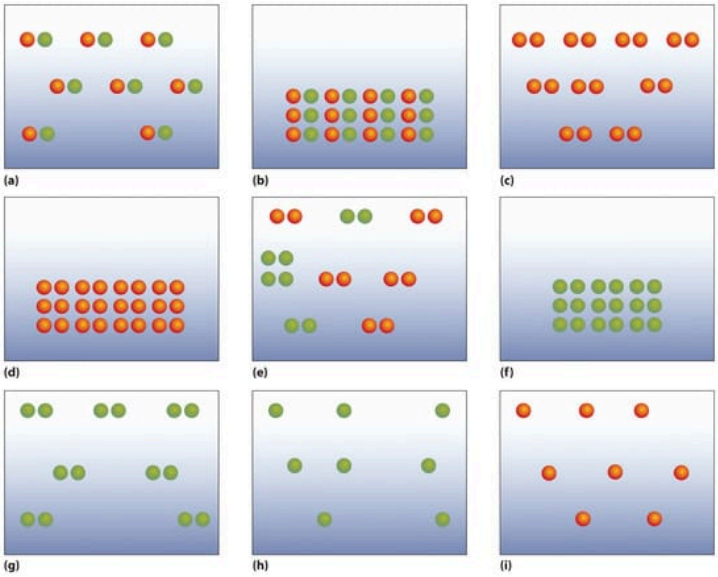
CONCEPTUAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9) before proceeding to the Conceptual Problems.

1. What is the difference between mass and weight? Is the mass of an object on Earth the same as the mass of the same object on Jupiter? Why or why not?
2. Is it accurate to say that a substance with a mass of 1 kg weighs 2.2 lb? Why or why not?
3. What factor must be considered when reporting the weight of an object as opposed to its mass?
4. Construct a table with the headings “Solid,” “Liquid,” and “Gas.” For any given substance, state what you expect for each of the following:
    1. the relative densities of the three phases
    2. the physical shapes of the three phases
    3. the volumes for the same mass of compound
    4. the sensitivity of the volume of each phase to changes in temperature
    5. the sensitivity of the volume to changes in pressure
5. Classify each substance as homogeneous or heterogeneous and explain your reasoning.
    1. platinum
    2. a carbonated beverage
    3. bronze
    4. wood
    5. natural gas
    6. Styrofoam
6. Classify each substance as homogeneous or heterogeneous and explain your reasoning.
    1. snowflakes
    2. gasoline
    3. black tea
    4. plastic wrap
    5. blood
    6. water containing ice cubes
7. Classify each substance as a pure substance or a mixture and explain your reasoning.
    1. seawater
    2. coffee
    3. 14-karat gold
    4. diamond
    5. distilled water
8. Classify each substance as a pure substance or a mixture.
    1. cardboard
    2. caffeine
    3. tin
    4. a vitamin tablet
    5. helium gas
9. Classify each substance as an element or a compound.
    1. sugar
    2. silver

3. rust
4. rubbing alcohol
5. copper

10. Classify each substance as an element or a compound.
    1. water
    2. iron
    3. hydrogen gas
    4. glass
    5. nylon
11. What techniques could be used to separate each of the following?
    1. sugar and water from an aqueous solution of sugar
    2. a mixture of sugar and sand
    3. a heterogeneous mixture of solids with different solubilities
12. What techniques could be used to separate each of the following?
    1. solid calcium chloride from a solution of calcium chloride in water
    2. the components of a solution of vinegar in water
    3. particulates from water in a fish tank
13. Match each separation technique in (a) with the physical/chemical property that each takes advantage of in (b).
    1. crystallization, distillation, filtration
    2. volatility, physical state, solubility
14. The following figures illustrate the arrangement of atoms in some samples of matter. Which figures are related by a physical change? By a chemical change?



15. Classify each statement as an extensive property or an intensive property.
    1. Carbon, in the form of diamond, is one of the hardest known materials.
    2. A sample of crystalline silicon, a grayish solid, has a mass of 14.3 g.
    3. Germanium has a density of 5.32 g/cm3.
    4. Gray tin converts to white tin at 13.2°C.
    5. Lead is a bluish-white metal.
16. Classify each statement as a physical property or a chemical property.
    1. Fluorine etches glass.
    2. Chlorine interacts with moisture in the lungs to produce a respiratory irritant.
    3. Bromine is a reddish-brown liquid.
    4. Iodine has a density of 11.27 g/L at 0°C.

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9) before proceeding to the Numerical Problems.

1. If a person weighs 176 lb on Earth, what is his or her mass on Mars, where the force of gravity is 37% of that on Earth?
2. If a person weighs 135 lb on Earth, what is his or her mass on Jupiter, where the force of gravity is 236% of that on Earth?
3. Calculate the volume of 10.00 g of each element and then arrange the elements in order of decreasing volume. The numbers in parentheses are densities.
    1. copper (8.92 g/cm3)
    2. calcium (1.54 g/cm3)
    3. titanium (4.51 g/cm3)
    4. iridium (22.85 g/cm3)
4. Given 15.00 g of each element, calculate the volume of each and then arrange the elements in order of increasing volume. The numbers in parentheses are densities.
    1. gold (19.32 g/cm3)
    2. lead (11.34 g/cm3)
    3. iron (7.87 g/cm3)
    4. sulfur (2.07 g/cm3)
5. A silver bar has dimensions of 10.00 cm × 4.00 cm × 1.50 cm, and the density of silver is 10.49 g/cm3. What is the mass of the bar?
6. Platinum has a density of 21.45 g/cm3. What is the mass of a platinum bar measuring 3.00 cm × 1.50 cm × 0.500 cm?
7. Complete the following table.

Density (g/cm3)	Mass (g)	Volume (cm3)	Element
3.14	79.904		Br
3.51		3.42	C
	39.1	45.5	K
11.34	207.2		Pb
	107.868	10.28	Ag
6.51		14.0	Zr

8. Gold has a density of 19.30 g/cm3. If a person who weighs 85.00 kg (1 kg = 1000 g) were given his or her weight in gold, what volume (in cm3) would the gold occupy? Are we justified in using the SI unit of mass for the person's weight in this case?
9. An irregularly shaped piece of magnesium with a mass of 11.81 g was dropped into a graduated cylinder partially filled with water. The magnesium displaced 6.80 mL of water. What is the density of magnesium?
10. The density of copper is 8.92 g/cm3. If a 10.00 g sample is placed in a graduated cylinder that contains 15.0 mL of water, what is the total volume that would be occupied?
11. At 20°C, the density of fresh water is 0.9982 kg/m3, and the density of seawater is 1.025 kg/m3. Will a ship float higher in fresh water or in seawater? Explain your reasoning.

Numerical Answers

1. Unlike weight, mass does not depend on location. The mass of the person is therefore the same on Earth and Mars: 176 lb ÷ 2.2 lb/kg = 80 kg.

3.

a. Cu: 1.12 cm^3

b. Ca: 6.49 cm^3

c. Ti: 2.22 cm^3

d. Ir: 0.4376 cm^3

Volume decreases: Ca > Ti > Cu > Ir

5. 629 g

9. 1.74 g/cm^3

1.3 Problems

1. Milk turns sour. This is a _____

- Chemical Change
- Physical Change
- Chemical Property
- Physical Property
- None of the above

2. HCl being a strong acid is a _____, Wood sawed in two is _____

- Chemical Change, Physical Change
- Physical Change, Chemical Change
- Chemical Property, Physical Change
- Physical Property, Chemical Change
- None of the above

3. $CuSO_4$ is dissolved in water

- Chemical Change
- Physical Change
- Chemical Property
- Physical Property
- None of the above

4. Aluminum Phosphate has a density of 2.566 g/cm3

- Chemical Change
- Physical Change
- Chemical Property
- Physical Property
- None of the above

5. Which of the following are examples of matter?

- A Dog
- Carbon Dioxide
- Ice Cubes
- copper (II) nitrate
- A Moving Car

6. The formation of gas bubbles is a sign of what type of change?

7. True or False: Bread rising is a physical property. 8. True or False: Dicing potatoes is a physical change. 9. Is sunlight matter? 10. The mass of lead is a _____property.

1.3 Solutions

1)chemical change 2) chemical property, physical change 3) physical change 4) physical property 5) All of the above 6) chemical 7) False 8) True 9) No 10) physical property

1.6

1. Write a single equation to show how to convert
   a. cm/min to km/h;
   b. cal/oz to J/g
   c. lb/in^2 to kg/m^2 and
   d. $°C/s$ to K/h.
2. How many Calories are contained in an 8.0 oz serving of green beans if their fuel value is 1.5 kJ/g?
3. Gasoline has a fuel value of 48 kJ/g. How much energy in joules can be obtained by filling an automobile's 16.3 gal tank with gasoline, assuming gasoline has a density of 0.70 g/mL?

Solutions

1. Converting from one compound unit to another
   a. $$\left(\frac{cm}{min}\right)\left(\frac{1\ m}{100\ cm}\right)\left(\frac{1\ km}{1000\ m}\right)\left(\frac{60\ min}{1\ h}\right) = km/h$$
   b. $$\left(\frac{cal}{oz}\right)\left(\frac{4.184\ J}{1\ cal}\right)\left(\frac{16\ oz}{1\ lb}\right)\left(\frac{1\ lb}{453.59\ g}\right) = J/g$$
   c. $$\left(\frac{lb}{in^2}\right)\left(\frac{16\ oz}{lb}\right)\left(\frac{28.35\ g}{oz}\right)\left(\frac{1\ kg}{1000\ g}\right)\left[\frac{(36\ in.)^2}{(1\ yd)^2}\right]\left[\frac{1.09\ yd^2}{1\ m^2}\right] = kg/m^2$$
   d. $$\left(\frac{°C}{s}\right)\left(\frac{60\ s}{1\ min}\right)\left(\frac{60\ min}{h}\right) + 273.15K = K/h$$
2. Our goal is to convert 1.5 kJ/g to Calories in 8 oz:
$$\left(\frac{1.5\ kJ}{1\ g}\right)\left(\frac{1000\ J}{1\ kJ}\right)\left(\frac{1\ cal}{4.184\ J}\right)\left(\frac{1\ Cal}{1000\ cal}\right)\left(\frac{28.35\ g}{1\ oz}\right)(8.0\ oz) = 81\ Cal$$
3. Our goal is to use the energy content, 48 kJ/g, and the density, 0.70 g/mL, to obtain the number of joules in 16.3 gal of gasoline:
$$\left(\frac{48\ kJ}{g}\right)\left(\frac{1000\ J}{kJ}\right)\left(\frac{0.70\ g}{mL}\right)\left(\frac{1000\ mL}{L}\right)\left(\frac{3.79\ L}{gal}\right)(16.3\ gal) = 2.1 \times 10^9 J$$

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1.S: Matter and Measurement (Summary)

1.1: The Study of Chemistry

An understanding of chemistry is essential for understanding much of the natural world and is central to many other disciplines. Chemistry is the study of matter and the changes material substances undergo. It is essential for understanding much of the natural world and central to many other scientific disciplines, including astronomy, geology, paleontology, biology, and medicine.

The Molecular Perspective of Chemistry

- **Matter** – physical material of the universe, has mass and takes up space
- **Atoms** – the building blocks of matter
- **Molecules** – groups of combined atoms

Why Study Chemistry?

- important in understanding our world
- chemistry is the central science
- many various subjects have some kind of relation to chemistry

1.2: Classification of Matter

Matter can be classified according to physical and chemical properties. Matter is anything that occupies space and has mass. The three states of matter are solid, liquid, and gas. A physical change involves the conversion of a substance from one state of matter to another, without changing its chemical composition. Most matter consists of mixtures of pure substances, which can be homogeneous (uniform in composition) or heterogeneous (different regions possess different compositions & properties.

States of Matter

- states of matter: liquid, solid, and gas

Pure Substances and Mixtures

- **pure substance** – matter that has a fixed composition and distinct properties
- substances can be classified as **elements** or **compounds**
- **elements** – composed of only one atom
- **compounds** – two ore more elements
- **mixtures** – combination of two or more substances
- **heterogeneous** – mixtures that are not uniform throughout
- **homogeneous** – mixtures that are uniform throughout; also called solutions

Separation of Mixtures

- components in a mixture retain their own properties
- mixtures can be separated by using the different properties of each substance
- types of separation: filtration, distillation, chromatography

Elements

- over 90% of earth's crust consists of oxygen, silicon, aluminum, iron, and calcium
- human body consists of 90% of oxygen, carbon, and hydrogen

Compounds

- **law of constant composition (law of definite proportions)** – elemental composition of a pure compound is always the same

1.3: Properties of Matter

All matter has physical and chemical properties. Physical properties are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). Chemical properties describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion.

- **physical properties** – properties measured by not changing the identity and composition of the substance
- **chemical properties** – the way a substance may change or react to form other substances
- **intensive properties** – identify substances
- **extensive properties** – amount of substance

Physical and Chemical Changes

- physical change results in a change in appearance but not composition
- changes of state are physical changes
- chemical changes (chemical reactions) results in a chemically different substance

1.4: Units of Measurement

The natural sciences begin with observation, and this usually involves numerical measurements of quantities such as length, volume, density, and temperature. Most of these quantities have units of some kind associated with them, and these units must be retained when you use them in calculations. Measuring units can be defined in terms of a very small number of fundamental ones that, through "dimensional analysis", provide insight into their derivation and meaning.

SI Units

- seven base units

SI Units

Prefix	Abbreviation	Meaning
Mega-	M	10^{6}
Kilo-	K	10^{3}
Deci-	D	10^{-1}
Centi-	C	10^{-2}
Milli-	m	10^{-3}
Micro-	μ^{a}	10^{-6}
Nano-	n	10^{-9}

Prefix	Abbreviation	Meaning
Pico-	p	10^{-12}
Femto-	f	10^{-15}

Length and Mass

- ◦ SI base unit for length is the meter (m)
  ◦ Mass is a measure of the amount of material in an object

Temperature

- Celsius and Kelvin scales are used commonly in science
- Both have equal sized units
- K = °C + 273.15
- °C = (5/9)(°F –32)
- °F = (9/5)(°C) + 32

Derived SI Units

Volume

- SI unit is cubic meter
- Equipment to measure volume accurately : syringes, burets, and pipets

Density

- density = mass/volume

1.5: Uncertainty in Measurement

Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal of scientists is to obtain measured values that are both accurate and precise.

1.5.1 Precision and Accuracy

- **precision** – the closeness of individual measurements to one another
- **accuracy** – the correctness of individual measurements

Significant Figures

- Nonzero digits are always significant
- Zeros between nonzero digits are always significant
- Zeros at the beginning of a number are never significant
- Zeros that fall both at the end of a number and after the decimal point are always significant
- When a number ends in zeros but contains no decimal point, the zeros may or may not be significant
- Scientific notation can be used to get the correct significant numbers

Significant Figures in Calculations

- Addition/Subtraction: the number of *decimal places* is determined by the number that has the fewest *decimal places* in the calculation
- Multiplication/Division: the number of *significant figures* is determined by the number that has the fewest *significant figures* in the calculation

1.6: Dimensional Analysis

Dimensional analysis is used in numerical calculations, and in converting units. It can help us identify whether an equation is set up correctly (i.e. the resulting units should be as expected). Units are treated similarly to the associated numerical values, i.e., if a variable in an equation is supposed to be squared, then the associated dimensions are squared, etc.

- aid in problem solving
- conversion factor – fraction where the numerator and denominator are the same quantity

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2: ATOMS, MOLECULES, AND IONS

In this chapter, you will learn how to describe the composition of chemical compounds. We introduce *chemical nomenclature*—the language of chemistry—that will enable you to recognize and name the most common kinds of compounds. An understanding of chemical nomenclature not only is essential for your study of chemistry but also has other benefits—for example, it helps you understand the labels on products found in the supermarket and the pharmacy. You will also be better equipped to understand many of the important environmental and medical issues that face society. By the end of this chapter, you will be able to describe what happens chemically when a doctor prepares a cast to stabilize a broken bone, and you will know the composition of common substances such as laundry bleach, the active ingredient in baking powder, and the foul-smelling compound responsible for the odor of spoiled fish. Finally, you will be able to explain the chemical differences among different grades of gasoline.

2.1: The Atomic Theory of Matter

2.2: The Discovery of Atomic Structure

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2.S: Atoms, Molecules, and Ions (Summary)

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2.1: The Atomic Theory of Matter

Learning Objectives

- Explain how all matter is composed of atoms.
- Describe the modern atomic theory.

Take some aluminum foil. Cut it in half. Now there are two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil. It should be obvious that the pieces are still aluminum foil; they are just becoming smaller and smaller. But how far can this exercise be taken, at least in theory? Can one continue cutting the aluminum foil into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of aluminum foil? Thought experiments like this—and the conclusions based on them—were debated as far back as the fifth century BC.

John Dalton (1766-1844) is the scientist credited for proposing the atomic theory. The theory explains several concepts that are relevant in the observable world: the composition of a pure gold necklace, what makes the pure gold necklace different than a pure silver necklace, and what occurs when pure gold is mixed with pure copper. This section explains the theories that Dalton used as a basis for his theory: (1) Law of Conservation of Mass, (2) Law of Definite Proportions, and (3) Law of Multiple Proportions

Law 1: The Conservation of Mass

"Nothing comes from nothing" is an important idea in ancient Greek philosophy that argues that what exists **now** has always **existed**, since no new matter can come into existence where there was none before. Antoine Lavoisier (1743-1794) restated this principle for chemistry with the law of conservation of mass, which "means that the atoms of an object cannot be created or destroyed, but can be moved around and be changed into different particles." This law says that when a chemical reaction rearranges atoms into a new product, the mass of the reactants (chemicals before the chemical reaction) is the same as the mass of the products (the new chemicals made). More simply, whatever you do, you will still have the same amount of stuff (however, certain nuclear reactions like fusion and fission can convert a small part of the mass into energy.

The law of conservation of mass states that the total mass present before a chemical reaction is the same as the total mass present after the chemical reaction; in other words, **mass is conserved**. The law of conservation of mass was formulated by Lavoisier as a result of his combustion experiment, in which he observed that the mass of his original substance—a glass vessel, tin, and air—was equal to the mass of the produced substance—the glass vessel, “tin calx”, and the remaining air.

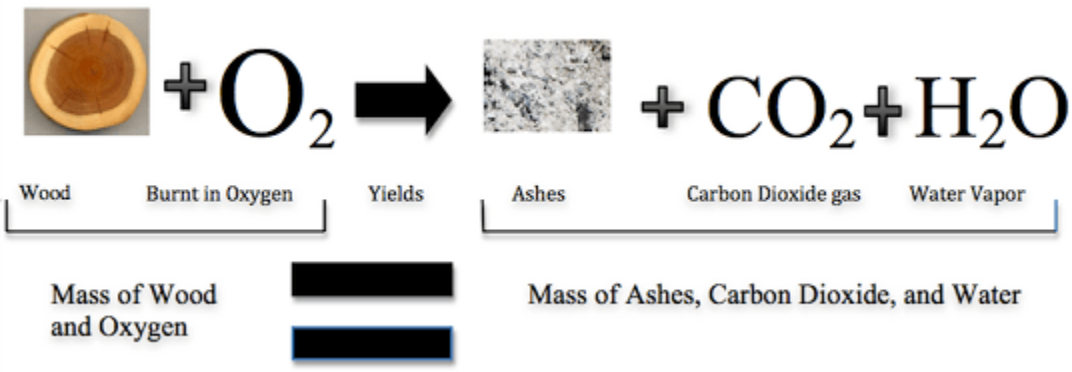


Figure 2.1.1: Image of the wood courtesy of Ehamberg and Stannered on Wikimedia Commons, available under Creative Commons Attribution 2.5 Generic license. Image of ashes courtesy of Walter Siegmund. Image as a whole constructed by Jessica Thornton (UCD).

Chemical equation; wood + oxygen yields ashes + carbon dioxide gas + water vapor. The mass of wood and oxygen equals the mass of ashes, carbon dioxide, and water.

Historically, this was a difficult concept for scientists to grasp. If this law was true, then how could a large piece of wood be reduced to a small pile of ashes? The wood clearly has a greater mass than the ashes. From this observation scientists concluded

that mass had been lost. However, Figure 2.1.1 shows that the burning of word does follow the law of conservation of mass. Scientists did not account for the gases that play a critical role in this reaction.

> The law of conservation of mass states that the total mass present before a chemical reaction is the same as the total mass present after the chemical reaction.

Law 2: Definite Proportions

Joseph Proust (1754-1826) formulated the *law of definite proportions* (also called the **Law of Constant *Composition*** or **Proust's Law**). This law states that if a compound is broken down into its constituent elements, the masses of the constituents will always have the same proportions, regardless of the quantity or source of the original substance. Joseph Proust based this law primarily on his experiments with basic copper carbonate. The illustration below depicts this law in action.

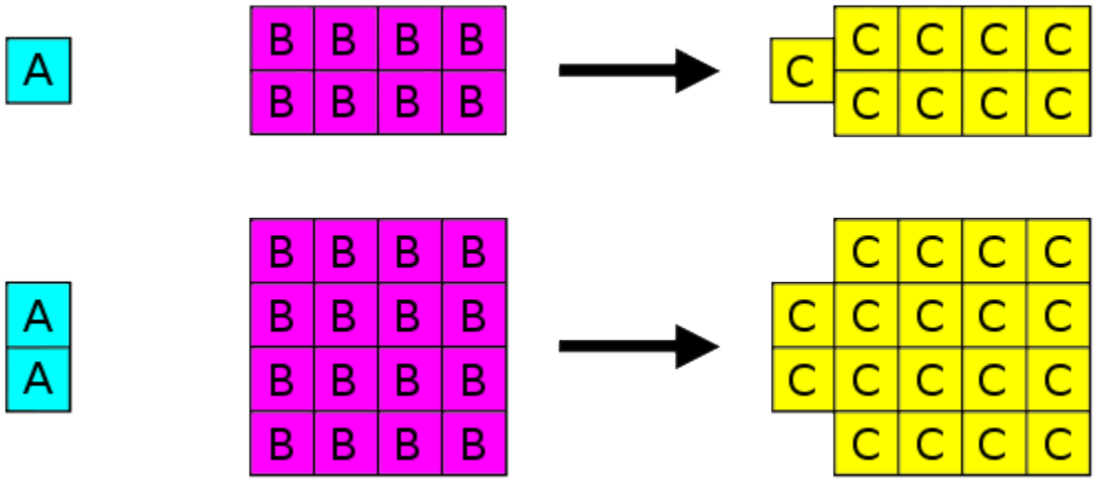


Figure 2.1.2: If 1 gram of A reacts with 8 grams of B, then by the Law of Definite Proportions, 2 grams of A must react with 16 grams of B. If 1 gram of A reacts with 8 grams of B, then by the Law of Conservation of Mass, they must produce 9 grams of C. Similarly, when 2 grams of A react with 16 grams of B, they must produce 18 grams of C.

Top: Single block labelled A. Eight blocks labelled B with arrow pointing to nine blocks labelled C. Bottom: Two blocks labelled A. Sixteen blocks labelled B with arrow pointing to eighteen blocks labelled C.

> Law of Definite Proportions states that in a given type of chemical substance, the elements are always combined in the same proportions by mass.

The Law of Definite Proportions applies when elements are reacted together to form *the same* product. Therefore, while the Law of Definite Proportions can be used to compare two experiments in which hydrogen and oxygen react to form water, the Law of Definite Proportions can *not* be used to compare one experiment in which hydrogen and oxygen react to form water, and another experiment in which hydrogen and oxygen react to form hydrogen peroxide (peroxide is another material that can be made from hydrogen and oxygen).

Example 2.1.1: water

Oxygen makes up 88.8% of the mass of any sample of pure water, while hydrogen makes up the remaining 11.2% of the mass. You can get water by melting ice or snow, by condensing steam, from river, sea, pond, etc. It can be from different places: USA, UK, Australia, or anywhere. It can be made by chemical reactions like burning hydrogen in oxygen.

However, if the water is **pure**, it will **always** consist of 88.8 % oxygen by mass and 11.2 % hydrogen by mass, irrespective of its source or method of preparation.

Law 3: Multiple Proportions

Many combinations of elements can react to form more than one compound. In such cases, this law states that the weights of one

element that combine with a fixed weight of another of these elements are integer multiples of one another. It's easy to say this, but please make sure that you understand how it works. Nitrogen forms a very large number of oxides, five of which are shown here.

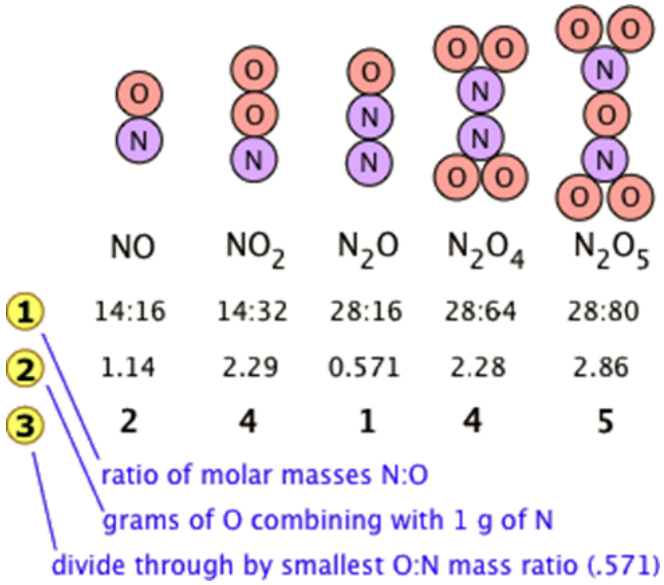


Figure 2.1.3: Law of Multiple Proportions applied to nitrogen oxides (NO_x) compounds. Table of several nitrogen-oxygen compounds. Column headings, left to right: N O, N O 2, N 2 O, N 2 O 4, N 2 O 5. Second row heading: ratio of molar masses N:O. Values, left to right: 14:16, 14:32, 28:16, 28:64, 28:80. Second row heading: grams of O combining with 1 gram of N. Values: 1.14, 2.29, 0.571, 2.28, 2.86. Third row heading: divide through by smallest O:N mass ratio (.571). Values: 2, 4, 1, 4, 5. (CC-BY; Stephen Lower)

- Line 1 shows the ratio of the relative weights of the two elements in each compound. These ratios were calculated by simply taking the molar mass of each element, and multiplying by the number of atoms of that element per mole of the compound. Thus for NO_2, we have (1 × 14) : (2 × 16) = 14:32. (These numbers were not known in the early days of Chemistry because atomic weights (i.e., molar masses) of most elements were not reliably known.)
- The numbers in Line 2 are just the mass ratios of O:N, found by dividing the corresponding ratios in line 1. But someone who depends solely on experiment would work these out by finding the mass of O that combines with unit mass (1 g) of nitrogen.
- Line is obtained by dividing the figures the previous line by the smallest O:N ratio in the line above, which is the one for N_2O. Note that just as the law of multiple proportions says, the weight of oxygen that combines with unit weight of nitrogen work out to small integers.
- Of course we just as easily could have illustrated the law by considering the mass of nitrogen that combines with one gram of oxygen; it works both ways!

> The law of multiple proportions states that if two elements form more than one compound between them, the masses of one element combined with a fixed mass of the second element form in ratios of small integers.

Example 2.1.2: Oxides of Carbon

Consider two separate compounds are formed by only carbon and oxygen. The first compound contains 42.9% carbon and 57.1% oxygen (by mass) and the second compound contains 27.3% carbon and 72.7% oxygen (again by mass). Is this consistent with the law of multiple proportions?

Solution

The *Law of Multiple Proportions* states that the masses of one element which combine with a fixed mass of the second element are in a ratio of **whole** numbers. Hence, the masses of oxygen in the two compounds that combine with a fixed mass of carbon should be in a whole-number ratio.

Thus for every 1 g of the first compound there are 0.57 g of oxygen and 0.429 g of carbon. The mass of oxygen per gram carbon is:

$$\frac{0.571 \text{ g oxygen}}{0.429 \text{ g carbon}} = 1.33 \frac{\text{g oxygen}}{\text{g carbon}}$$

Similarly, for 1 g of the second compound, there are 0.727 g oxygen and 0.273 g of carbon. The ration of mass of oxygen per gram of carbon is

$$\frac{0.727 \text{ g oxygen}}{0.273 \text{ g carbon}} = 2.66 \frac{\text{g oxygen}}{\text{g carbon}}$$

Dividing the mass of oxygen per g of carbon of the second compound:

$$\frac{2.66}{1.33} = 2$$

Hence the masses of oxygen combine with carbon in a 2:1 ratio which s consistent with the Law of Multiple Proportions since they are whole numbers.

Dalton's Atomic Theory

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 2.1.4), is a fundamental concept that states that all elements are composed of atoms. Previously, an atom was defined as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of the human pinkie (about 1 cm).

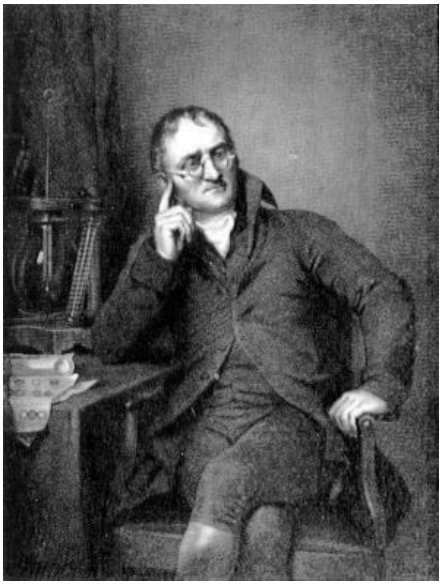


Figure 2.1.4: John Dalton was an English scientist who enunciated the modern atomic theory.

Dalton's ideas are called the *modern* atomic theory because the concept of atoms is very old. The Greek philosophers Leucippus and Democritus originally introduced atomic concepts in the fifth century BC. (The word *atom* comes from the Greek word *atomos*, which means "indivisible" or "uncuttable.") Dalton had something that the ancient Greek philosophers didn't have, however; he had experimental evidence, such as the formulas of simple chemicals and the behavior of gases. In the 150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was being used to study nature. When Dalton announced a modern atomic theory, he was proposing a fundamental theory to describe many previous observations of the natural world; he was not just participating in a philosophical discussion.

Dalton's Theory was a powerful development as it explained the three laws of chemical combination (above) and recognized a

workable distinction between the fundamental particle of an element (atom) and that of a compound (molecule). Six postulates are involved in Dalton's Atomic Theory:

1. All matter consists of indivisible particles called atoms.
2. Atoms of the same element are similar in shape and mass, but differ from the atoms of other elements.
3. Atoms cannot be created or destroyed.
4. Atoms of different elements may combine with each other in a fixed, simple, whole number ratios to form compound atoms.
5. Atoms of same element can combine in more than one ratio to form two or more compounds.
6. The atom is the smallest unit of matter that can take part in a chemical reaction.

In light of the current state of knowledge in the field of Chemistry, Dalton's theory had a few drawbacks. According to Dalton's postulates,

1. The indivisibility of an atom was proved wrong: an atom can be further subdivided into protons, neutrons and electrons. However an atom is the smallest particle that takes part in chemical reactions.
2. According to Dalton, the atoms of same element are similar in all respects. However, atoms of some elements vary in their masses and densities. These atoms of different masses are called isotopes. For example, chlorine has two isotopes with mass numbers 35 and 37.
3. Dalton also claimed that atoms of different elements are different in all respects. This has been proven wrong in certain cases: argon and calcium atoms each have an same atomic mass (40 amu).
4. According to Dalton, atoms of different elements combine in simple whole number ratios to form compounds. This is not observed in complex organic compounds like sugar ($C_{12}H_{22}O_{11}$).
5. The theory fails to explain the existence of allotropes (different forms of pure elements); it does not account for differences in properties of charcoal, graphite, diamond.

Despite these drawbacks, the importance of Dalton's theory should not be underestimated. He displayed exceptional insight into the nature of matter. and his ideas provided a framework that was later modified and expanded by other. Consequentiually, John Dalton is often considered to be the father of modern atomic theory.

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Fundamental Experiments in Chemistry: Fundamental Experiments in Chemistry, YouTube(opens in new window) [youtu.be]

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Summary

This article explains the theories that Dalton used as a basis for his theory: (1) the Law of Conservation of Mass, (2) the Law of Constant Composition, (3) the Law of Multiple Proportions.

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2.2: The Discovery of Atomic Structure

Learning Objectives

- To become familiar with the components and structure of the atom.

Long before the end of the 19th century, it was well known that applying a high voltage to a gas contained at low pressure in a sealed tube (called a gas discharge tube) caused electricity to flow through the gas, which then emitted light (Figure 2.2.1). Researchers trying to understand this phenomenon found that an unusual form of energy was also emitted from the cathode, or negatively charged electrode; this form of energy was called a cathode ray.

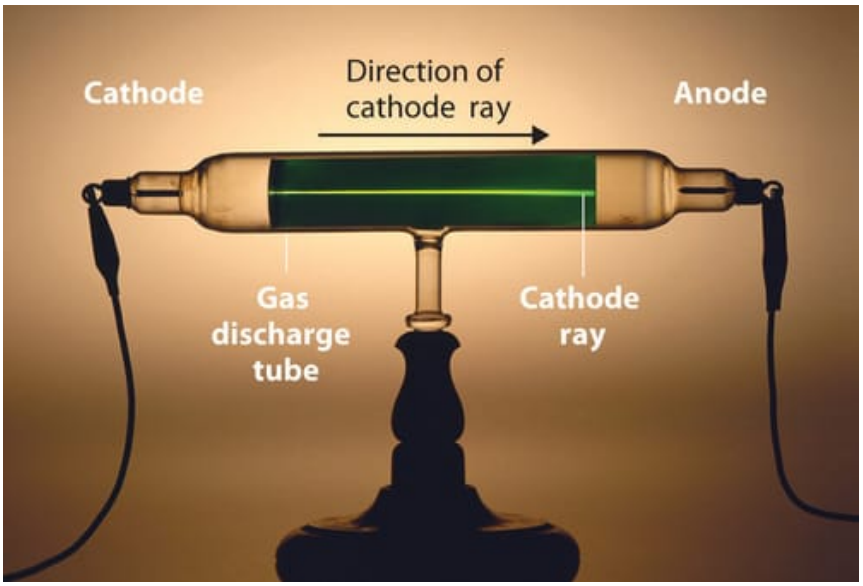


Figure 2.2.1: A Gas Discharge Tube Producing Cathode Rays. When a high voltage is applied to a gas contained at low pressure in a gas discharge tube, electricity flows through the gas, and energy is emitted in the form of light. Image used with Permission (CC BY-SA-NC).

In 1897, the British physicist J. J. Thomson (1856–1940) proved that atoms were not the most basic form of matter. He demonstrated that cathode rays could be deflected, or bent, by magnetic or electric fields, which indicated that cathode rays consist of charged particles (Figure 2.2.2). More important, by measuring the extent of the deflection of the cathode rays in magnetic or electric fields of various strengths, Thomson was able to calculate the mass-to-charge ratio of the particles. These particles were emitted by the negatively charged cathode and repelled by the negative terminal of an electric field. Because like charges repel each other and opposite charges attract, Thomson concluded that the particles had a net negative charge; these particles are now called electrons. Most relevant to the field of chemistry, Thomson found that the mass-to-charge ratio of cathode rays is independent of the nature of the metal electrodes or the gas, which suggested that electrons were fundamental components of all atoms.

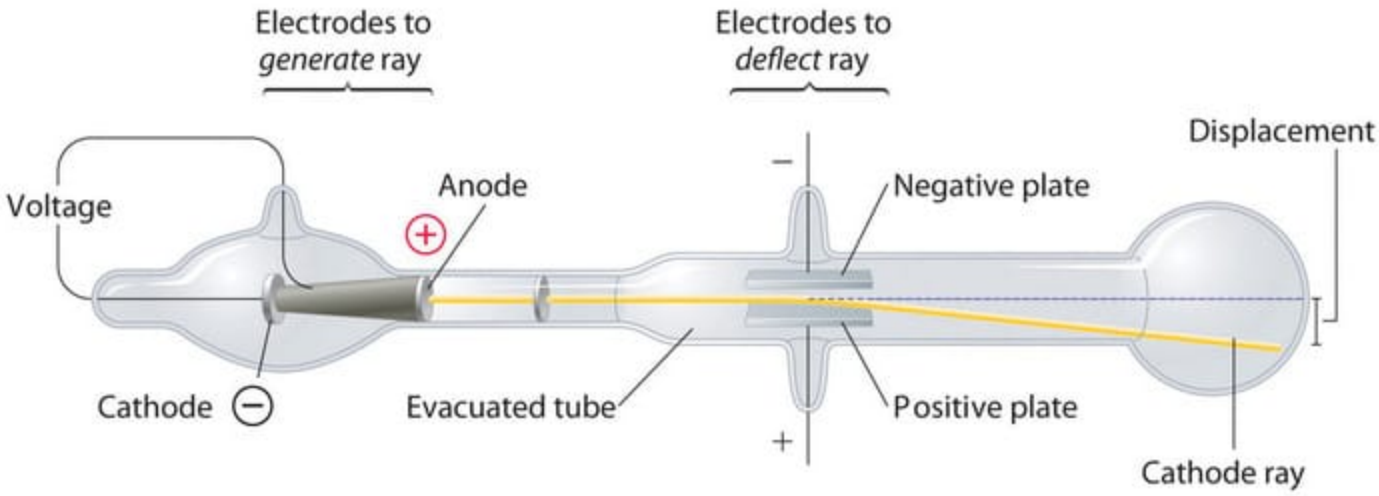


Figure 2.2.2: Deflection of Cathode Rays by an Electric Field. As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged. Image used with Permission (CC BY-SA-NC).

Schematic of cathode ray tube with deflection. Electrodes generate the ray. Another set of electrode plates deflect the ray, with the ray bending towards the positive plate.

Subsequently, the American scientist Robert Millikan (1868–1953) carried out a series of experiments using electrically charged oil droplets, which allowed him to calculate the charge on a single electron. With this information and Thomson's mass-to-charge ratio, Millikan determined the mass of an electron:

$$\frac{mass}{charge} \times charge = mass$$

It was at this point that two separate lines of investigation began to converge, both aimed at determining how and why matter emits energy. The video below shows how JJ Thompson used such a tube to measure the ratio of charge over mass of an electron

YouTube Video

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Measuring e/m For an Electron. Video from Davidson College demonstrating Thompson's e/m experiment.

Radioactivity

The second line of investigation began in 1896, when the French physicist Henri Becquerel (1852–1908) discovered that certain minerals, such as uranium salts, emitted a new form of energy. Becquerel's work was greatly extended by Marie Curie (1867–1934) and her husband, Pierre (1854–1906); all three shared the Nobel Prize in Physics in 1903. Marie Curie coined the term radioactivity (from the Latin *radius*, meaning "ray") to describe the emission of energy rays by matter. She found that one particular uranium ore, pitchblende, was substantially more radioactive than most, which suggested that it contained one or more highly radioactive impurities. Starting with several tons of pitchblende, the Curies isolated two new radioactive elements after months of work: polonium, which was named for Marie's native Poland, and radium, which was named for its intense radioactivity. Pierre Curie carried a vial of radium in his coat pocket to demonstrate its greenish glow, a habit that caused him to become ill from radiation poisoning well before he was run over by a horse-drawn wagon and killed instantly in 1906. Marie Curie, in turn, died of what was almost certainly radiation poisoning.

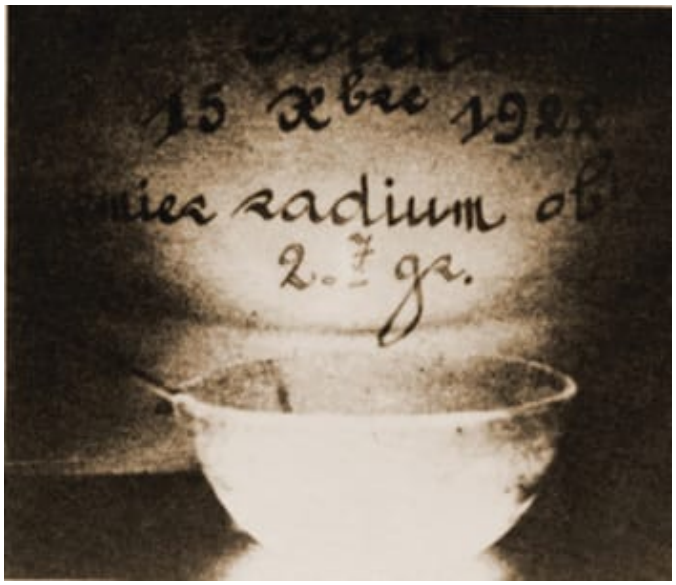


Figure 2.2.3: Radium bromide illuminated by its own radioactive glow. This 1922 photo was taken in the dark in the Curie laboratory.

Building on the Curies' work, the British physicist Ernest Rutherford (1871–1937) performed decisive experiments that led to the modern view of the structure of the atom. While working in Thomson's laboratory shortly after Thomson discovered the electron, Rutherford showed that compounds of uranium and other elements emitted at least two distinct types of radiation. One was readily absorbed by matter and seemed to consist of particles that had a positive charge and were massive compared to electrons. Because it was the first kind of radiation to be discovered, Rutherford called these substances α particles. Rutherford also showed that the particles in the second type of radiation, β particles, had the same charge and mass-to-charge ratio as Thomson's electrons; they are now known to be high-speed electrons. A third type of radiation, γ rays, was discovered somewhat later and found to be similar to the lower-energy form of radiation called x-rays, now used to produce images of bones and teeth.

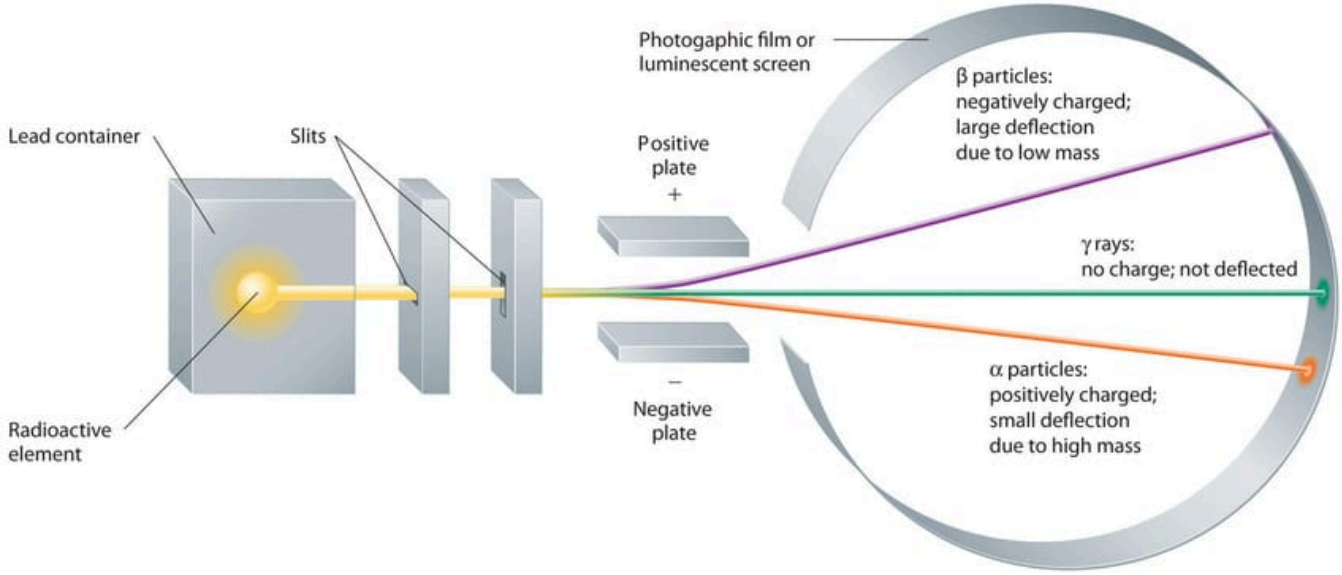


Figure 2.2.4: Effect of an Electric Field on α Particles, β Particles, and γ Rays. A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown to scale.) Image used with Permission (CC BY-SA-NC).

Schematic of a radioactive element in a lead container projected through slits to produce a narrow beam that impacts a photographic film. Two plates, one positive and one negative, deflect the beam depending on whether it is beta, gamma, or alpha. Beta particles deflect towards the positive plate and have a large deflection due to small mass. Alpha particles deflect towards the negative plate and have a small deflection due to high mass. Gamma rays do not deflect.

These three kinds of radiation—α particles, β particles, and γ rays—are readily distinguished by the way they are deflected by an electric field and by the degree to which they penetrate matter. As Figure 2.2.3 illustrates, α particles and β particles are

deflected in opposite directions; α particles are deflected to a much lesser extent because of their higher mass-to-charge ratio. In contrast, γ rays have no charge, so they are not deflected by electric or magnetic fields. Figure 2.2.5 shows that α particles have the least penetrating power and are stopped by a sheet of paper, whereas β particles can pass through thin sheets of metal but are absorbed by lead foil or even thick glass. In contrast, γ-rays can readily penetrate matter; thick blocks of lead or concrete are needed to stop them.

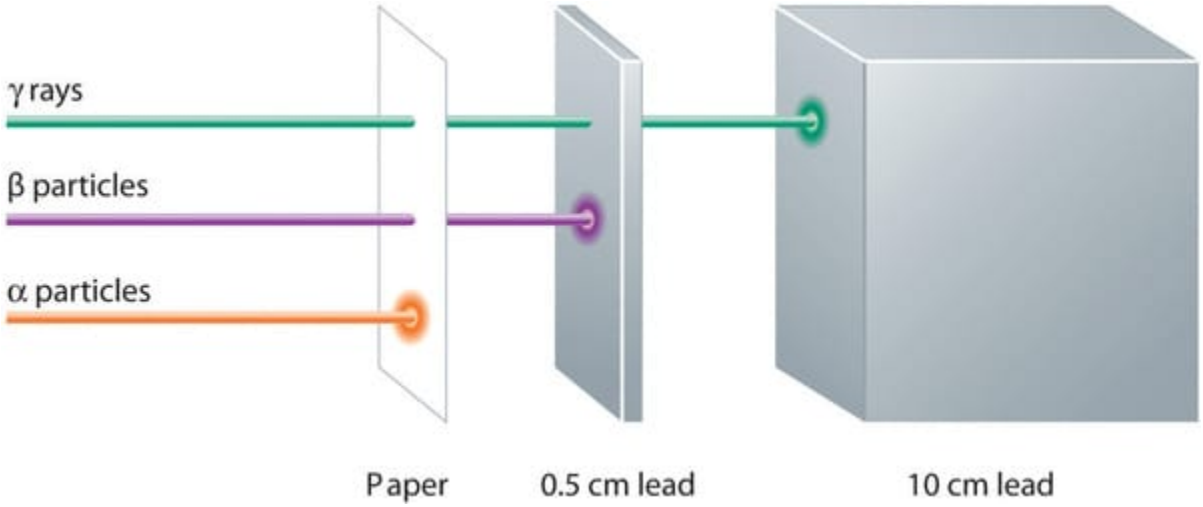


Figure 2.2.5: Relative Penetrating Power of the Three Types of Radiation. A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead or concrete is needed to absorb them. Image used with Permission (CC BY-SA-NC).

Cartoon of gamma, alpha, and beta rays. The beta ray is stopped by paper. The alpha ray is stopped by .5 centimeter lead. The gamma ray is stopped by 10 centimeter lead.

The Atomic Model

Once scientists concluded that all matter contains negatively charged electrons, it became clear that atoms, which are electrically neutral, must also contain positive charges to balance the negative ones. Thomson proposed that the electrons were embedded in a uniform sphere that contained both the positive charge and most of the mass of the atom, much like raisins in plum pudding or chocolate chips in a cookie (Figure 2.2.6).

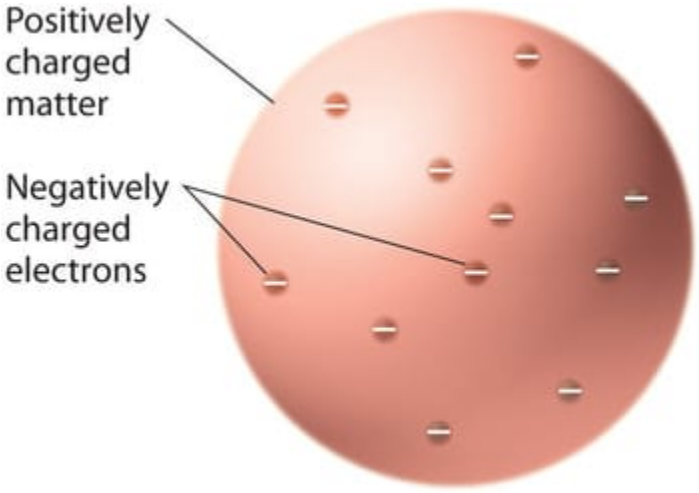


Figure 2.2.6: Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom. In this model, the electrons are embedded in a uniform sphere of positive charge. Image used with Permission (CC BY-SA-NC).

Diagram of the plum-pudding model, with spheres of negatively charged electrons in a larger sphere of positively charged matter.

In a single famous experiment, however, Rutherford showed unambiguously that Thomson's model of the atom was incorrect. Rutherford aimed a stream of α particles at a very thin gold foil target (Figure 2.2.7a) and examined how the α particles were

scattered by the foil. Gold was chosen because it could be easily hammered into extremely thin sheets, minimizing the number of atoms in the target. If Thomson's model of the atom were correct, the positively-charged α particles should crash through the uniformly distributed mass of the gold target like cannonballs through the side of a wooden house. They might be moving a little slower when they emerged, but they should pass essentially straight through the target (Figure $2.2.7b$). To Rutherford's amazement, a small fraction of the α particles were deflected at large angles, and some were reflected directly back at the source (Figure $2.2.7c$). According to Rutherford, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

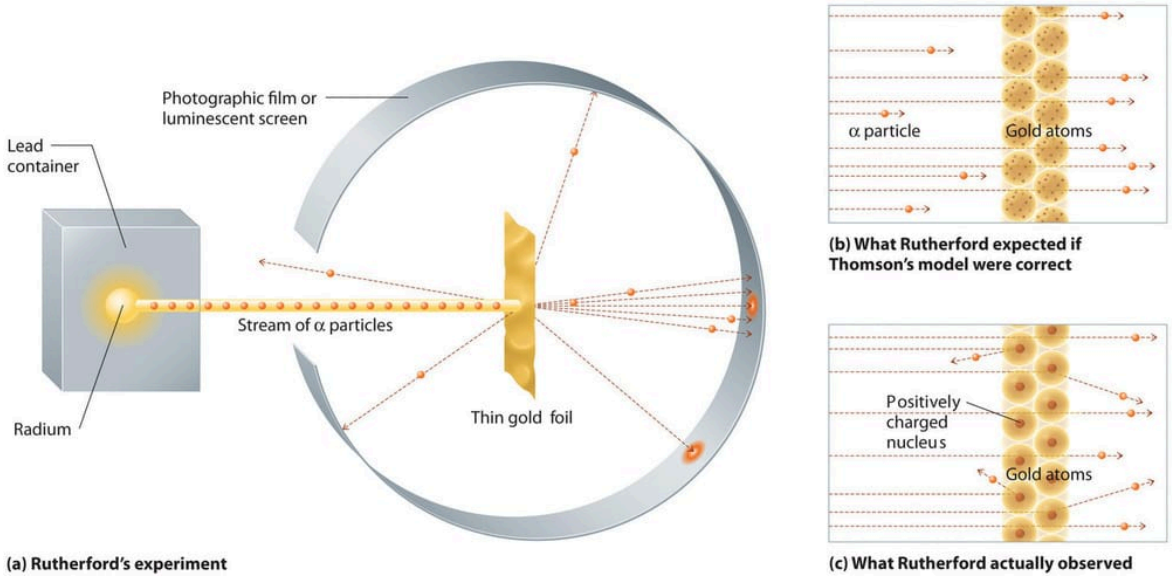


Figure $2.2.7$: A Summary of Rutherford's Experiments. (a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles should have passed straight through the gold foil. (c) However, a small number of α particles were deflected in various directions, including right back at the source. This could be true only if the positive charge were much more massive than the α particle. It suggested that the mass of the gold atom is concentrated in a very small region of space, which he called the nucleus. Image used with Permission (CC BY-SA-NC).

Schematic of Rutherford's gold foil experiment. Inset A: Radium fires a stream of alpha particles onto thin gold foil, showing particle deflection onto surrounding photographic film. Inset B: What Rutherford would have expected if Thomas' model were correct: alpha particles continuing through gold foil with no deflection. Inset C: What Rutherford actually observed: alpha particles deflected by nuclei of gold atoms.

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The Nuclear Atom: The Nuclear Atom, YouTube(opens in new window) [youtu.be]

Rutherford's results were not consistent with a model in which the mass and positive charge are distributed uniformly throughout the volume of an atom. Instead, they strongly suggested that both the mass and positive charge are concentrated in a tiny fraction of the volume of an atom, which Rutherford called the nucleus. It made sense that a small fraction of the α particles collided with the dense, positively charged nuclei in either a glancing fashion, resulting in large deflections, or almost head-on, causing them to be reflected straight back at the source.

Although Rutherford could not explain why repulsions between the positive charges in nuclei that contained more than one positive charge did not cause the nucleus to disintegrate, he reasoned that repulsions between negatively charged electrons would cause the electrons to be uniformly distributed throughout the atom's volume.Today it is known that strong nuclear forces, which are much stronger than electrostatic interactions, hold the protons and the neutrons together in the nucleus. For this and

other insights, Rutherford was awarded the Nobel Prize in Chemistry in 1908. Unfortunately, Rutherford would have preferred to receive the Nobel Prize in Physics because he considered physics superior to chemistry. In his opinion, “All science is either physics or stamp collecting.”

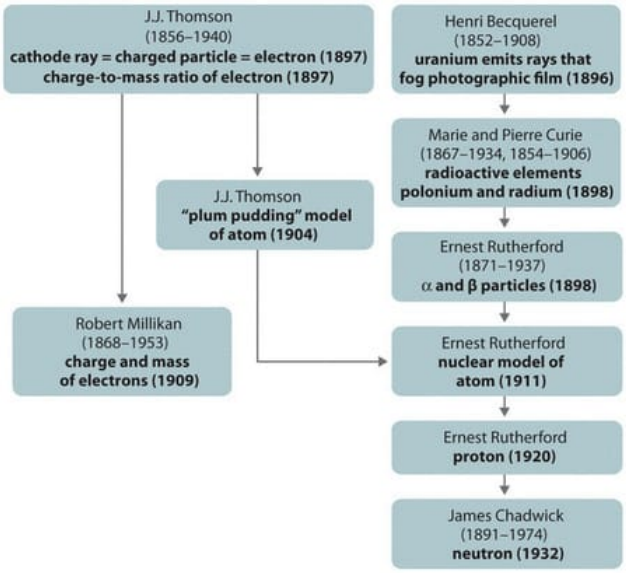


Figure 2.2.8: A Summary of the Historical Development of Models of the Components and Structure of the Atom. The dates in parentheses are the years in which the key experiments were performed. Image used with Permission (CC BY-SA-NC).

The historical development of the different models of the atom’s structure is summarized in Figure 2.2.8. Rutherford established that the nucleus of the hydrogen atom was a positively charged particle, for which he coined the name proton in 1920. He also suggested that the nuclei of elements other than hydrogen must contain electrically neutral particles with approximately the same mass as the proton. The neutron, however, was not discovered until 1932, when James Chadwick (1891–1974, a student of Rutherford; Nobel Prize in Physics, 1935) discovered it. As a result of Rutherford’s work, it became clear that an α particle contains two protons and neutrons, and is therefore the nucleus of a helium atom.

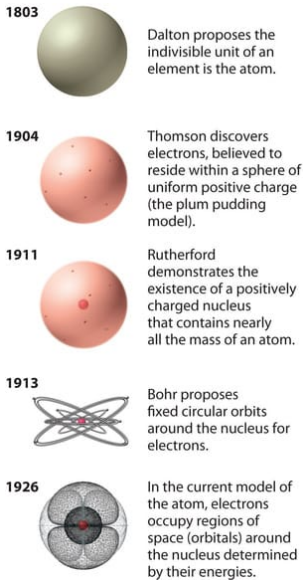


Figure 2.2.9: The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom. Bohr’s model and the current model are described in Chapter 6, "The Structure of Atoms." Image used with Permission (CC BY-SA-NC).

Summary timeline of the evolution of atomic theory. Shows events at 1803 with Dalton's original proposal, 1904 with Thomson's model, 1911 with Rutherford's experiment, 1913 with Bohr's model, and 1926 with the current orbital model of the atom.

Rutherford’s model of the atom is essentially the same as the modern model, except that it is now known that electrons are not uniformly distributed throughout an atom’s volume. Instead, they are distributed according to a set of principles described by

Quantum Mechanics. Figure 2.2.9 shows how the model of the atom has evolved over time from the indivisible unit of Dalton to the modern view taught today.

Summary

Atoms are the ultimate building blocks of all matter. The modern atomic theory establishes the concepts of atoms and how they compose matter. Atoms, the smallest particles of an element that exhibit the properties of that element, consist of negatively charged electrons around a central nucleus composed of more massive positively charged protons and electrically neutral neutrons. Radioactivity is the emission of energetic particles and rays (radiation) by some substances. Three important kinds of radiation are α particles (helium nuclei), β particles (electrons traveling at high speed), and γ rays (similar to x-rays but higher in energy).

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2.3: The Modern View of Atomic Structure

Learning Objectives

- To know the meaning of isotopes and atomic masses.

The precise physical nature of atoms finally emerged from a series of elegant experiments carried out between 1895 and 1915. The most notable of these achievements was Ernest Rutherford's famous 1911 alpha-ray scattering experiment, which established that

- Almost all of the *mass* of an atom is contained within a tiny (and therefore extremely dense) *nucleus* which carries a positive electric charge whose value identifies each element and is known as the *atomic number* of the element.
- Almost all of the *volume* of an atom consists of empty space in which electrons, the fundamental carriers of negative electric charge, reside. The extremely small mass of the electron (1/1840 the mass of the hydrogen nucleus) causes it to behave as a quantum particle, which means that its location at any moment cannot be specified; the best we can do is describe its behavior in terms of the probability of its manifesting itself at any point in space. It is common (but somewhat misleading) to describe the volume of space in which the electrons of an atom have a significant probability of being found as the *electron cloud*. The latter has no definite outer boundary, so neither does the atom. The radius of an atom must be defined arbitrarily, such as the boundary in which the electron can be found with 95% probability. Atomic radii are typically 30-300 pm.

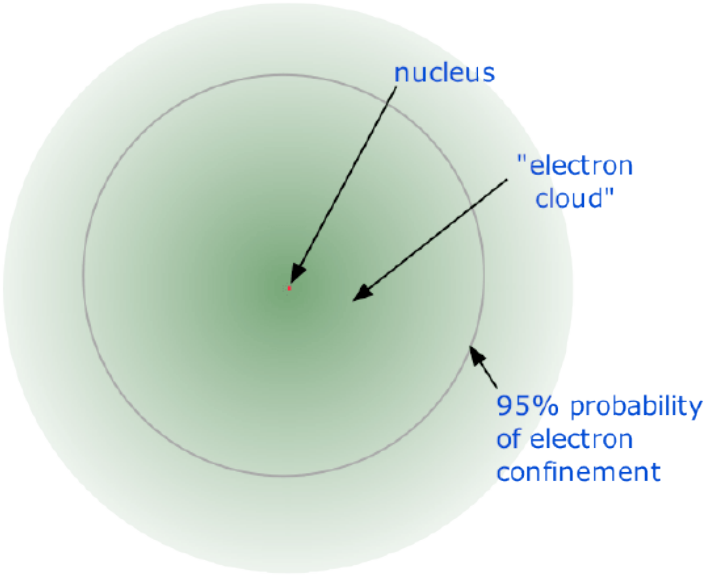


Figure 2.3.1: The structure of the nuclear atom with a central nucleus and surrounding electrons.

The nucleus is itself composed of two kinds of particles. *Protons* are the carriers of positive electric charge in the nucleus; the proton charge is exactly the same as the electron charge, but of opposite sign. This means that in any [electrically neutral] atom, the number of protons in the nucleus (often referred to as the *nuclear charge*) is balanced by the *same* number of electrons outside the nucleus. The other nuclear particle is the *neutron*. As its name implies, this particle carries no electrical charge. Its mass is almost the same as that of the proton. Most nuclei contain roughly equal numbers of neutrons and protons, so we can say that these two particles together account for almost all the mass of the atom.

> Because the electrons of an atom are in contact with the outside world, it is possible for one or more electrons to be lost, or some new ones to be added. The resulting electrically-charged atom is called an ion.

Elements

To date, about 115 different elements have been discovered; by definition, each is chemically unique. To understand why they

are unique, you need to understand the structure of the atom (the fundamental, individual particle of an element) and the characteristics of its components. Atoms consist of electrons, protons, and neutrons. Although this is an oversimplification that ignores the other subatomic particles that have been discovered, it is sufficient for discussion of chemical principles. Some properties of these subatomic particles are summarized in Table 2.3.1, which illustrates three important points:

1. Electrons and protons have electrical charges that are identical in magnitude but opposite in sign. Relative charges of –1 and +1 are assigned to the electron and proton, respectively.
2. Neutrons have approximately the same mass as protons but no charge. They are electrically neutral.
3. The mass of a proton or a neutron is about 1836 times greater than the mass of an electron. Protons and neutrons constitute the bulk of the mass of atoms.

The discovery of the electron and the proton was crucial to the development of the modern model of the atom and provides an excellent case study in the application of the scientific method. In fact, the elucidation of the atom's structure is one of the greatest detective stories in the history of science.

*Table 2.3.1: Properties of Subatomic Particles**

Particle	Mass (g)	Atomic Mass (amu)	Electrical Charge (coulombs)	Relative Charge
electron	9.109×10^{-28}	0.0005486	-1.602×10^{-19}	–1
proton	1.673×10^{-24}	1.007276	$+1.602 \times 10^{-19}$	+1
neutron	1.675×10^{-24}	1.008665	0	0

In most cases, the symbols for the elements are derived directly from each element's name, such as C for carbon, U for uranium, Ca for calcium, and Po for polonium. Elements have also been named for their properties [such as radium (Ra) for its radioactivity], for the native country of the scientist(s) who discovered them [polonium (Po) for Poland], for eminent scientists [curium (Cm) for the Curies], for gods and goddesses [selenium (Se) for the Greek goddess of the moon, Selene], and for other poetic or historical reasons. Some of the symbols used for elements that have been known since antiquity are derived from historical names that are no longer in use; only the symbols remain to indicate their origin. Examples are Fe for iron, from the Latin *ferrum*; Na for sodium, from the Latin *natrium*; and W for tungsten, from the German *wolfram*. Examples are in Table 2.3.2.

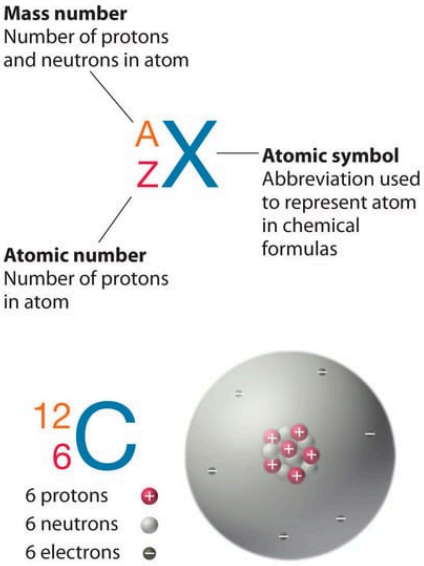
Table 2.3.2: Element Symbols Based on Names No Longer in Use

Element	Symbol	Derivation	Meaning
antimony	Sb	stibium	Latin for "mark"
copper	Cu	cuprum	from Cyprium, Latin name for the island of Cyprus, the major source of copper ore in the Roman Empire
gold	Au	aurum	Latin for "gold"
iron	Fe	ferrum	Latin for "iron"
lead	Pb	plumbum	Latin for "heavy"
mercury	Hg	hydrargyrum	Latin for "liquid silver"
potassium	K	kalium	from the Arabic al-qili, "alkali"
silver	Ag	argentum	Latin for "silver"
sodium	Na	natrium	Latin for "sodium"
tin	Sn	stannum	Latin for "tin"
tungsten	W	wolfram	German for "wolf stone" because it interfered with the smelting of tin and was thought to devour the tin

Recall that the nuclei of most atoms contain neutrons as well as protons. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called isotopes. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemistry. The isotopes of an element differ only in their atomic mass, which is given by the mass number (A),

the sum of the numbers of protons and neutrons.

The element carbon (C) has an atomic number of 6, which means that all neutral carbon atoms contain 6 protons and 6 electrons. In a typical sample of carbon-containing material, 98.89% of the carbon atoms also contain 6 neutrons, so each has a mass number of 12. An isotope of any element can be uniquely represented as ${}^{A}_{Z}X$, where X is the atomic symbol of the element. The isotope of carbon that has 6 neutrons is therefore ${}^{12}_{6}C$. The subscript indicating the atomic number is actually redundant because the atomic symbol already uniquely specifies Z. Consequently, ${}^{12}_{6}C$ is more often written as ^{12}C, which is read as "carbon-12." Nevertheless, the value of Z is commonly included in the notation for nuclear reactions because these reactions involve changes in Z.



Elaboration of atomic symbol, showing mass and atomic number next to symbol. Carbon-12 is shown as an example.

Figure 2.3.2*: Formalism used for identifying specific nuclide (any particular kind of nucleus)*

In addition to ${}^{12}C$, a typical sample of carbon contains 1.11% ${}^{13}_{6}C$ (^{13}C), with 7 neutrons and 6 protons, and a trace of ${}^{14}_{6}C$ (^{14}C), with 8 neutrons and 6 protons. The nucleus of ^{14}C is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archaeology. Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. The properties of some common isotopes are in Table 2.3.3.

Table 2.3.3*: Properties of Selected Isotopes*

Element	Symbol	Atomic Mass (amu)	Isotope Mass Number	Isotope Masses (amu)	Percent Abundances (%)
hydrogen	H	1.0079	1	1.007825	99.9855
			2	2.014102	0.0115
boron	B	10.81	10	10.012937	19.91
			11	11.009305	80.09
carbon	C	12.011	12	12 (defined)	99.89
			13	13.003355	1.11
oxygen	O	15.9994	16	15.994915	99.757
			17	16.999132	0.0378
			18	17.999161	0.205
iron	Fe	55.845	54	53.939611	5.82
			56	55.934938	91.66

Element	Symbol	Atomic Mass (amu)	Isotope Mass Number	Isotope Masses (amu)	Percent Abundances (%)
			57	56.935394	2.19
			58	57.933276	0.33
uranium	U	238.03	234	234.040952	0.0054
			235	235.043930	0.7204
			238	238.050788	99.274

Sources of isotope data: G. Audi et al., Nuclear Physics A 729 (2003): 337–676; J. C. Kotz and K. F. Purcell, Chemistry and Chemical Reactivity, 2nd ed., 1991.

YouTube Video

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How Elements Are Represented on the Periodic Table: How Elements Are Represented on the Periodic Table, YouTube(opens in new window) [youtu.be]

Example 2.3.1

An element with three stable isotopes has 82 protons. The separate isotopes contain 124, 125, and 126 neutrons. Identify the element and write symbols for the isotopes.

Given: number of protons and neutrons

Asked for: element and atomic symbol

Strategy:

A. Refer to the periodic table and use the number of protons to identify the element.
B. Calculate the mass number of each isotope by adding together the numbers of protons and neutrons.
C. Give the symbol of each isotope with the mass number as the superscript and the number of protons as the subscript, both written to the left of the symbol of the element.

Solution:

A The element with 82 protons (atomic number of 82) is lead: Pb.

B For the first isotope, A = 82 protons + 124 neutrons = 206. Similarly, A = 82 + 125 = 207 and A = 82 + 126 = 208 for the second and third isotopes, respectively. The symbols for these isotopes are $^{206}_{82}Pb$, $^{207}_{82}Pb$, and $^{208}_{82}Pb$, which are usually abbreviated as ^{206}Pb, ^{207}Pb, and ^{208}Pb.

Exercise 2.3.1

Identify the element with 35 protons and write the symbols for its isotopes with 44 and 46 neutrons.

Answer available at the end of this section.

Summary

The atom consists of discrete particles that govern its chemical and physical behavior. Each atom of an element contains the same number of protons, which is the **atomic number** (*Z*). Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number** (*A*), which is the sum of the numbers of protons and neutrons. The relative masses of atoms are reported using the **atomic mass unit** (**amu**), which is defined as one-twelfth of the mass of one atom of carbon-12, with 6 protons, 6 neutrons, and 6 electrons.

Answers

Exercise 2.3.1

$^{79}_{35}\mathrm{Br}$ and $^{81}_{35}\mathrm{Br}$ or, more commonly, $^{79}\mathrm{Br}$ and $^{81}\mathrm{Br}$.

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2.4: Atomic Mass

Learning Objectives

- to know the meaning of isotopes and atomic masses.

Atomic and Molecular Weights

The subscripts in chemical formulas, and the coefficients in chemical equations represent *exact* quantities. H_2O, for example, indicates that a water molecule comprises exactly **two** atoms of hydrogen and **one** atom of oxygen. The following equation:

$$C_3H_8\,(g) + 5\,O_2\,(g) \;\rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l) \tag{2.4.1}$$

not only tells us that propane reacts with oxygen to produce carbon dioxide and water, but that ***1*** molecule of propane reacts with ***5*** molecules of oxygen to produce ***3*** molecules of carbon dioxide and ***4*** molecules of water. Since counting individual atoms or molecules is a little difficult, quantitative aspects of chemistry rely on knowing the *masses* of the compounds involved.

Atoms of different elements have different masses. Early work on the separation of water into its constituent elements (hydrogen and oxygen) indicated that 100 grams of water contained 11.1 grams of hydrogen and 88.9 grams of oxygen:

$$100 \text{ grams Water} \rightarrow 11.1 \text{ grams Hydrogen} + 88.9 \text{ grams Oxygen} \tag{2.4.2}$$

Later, scientists discovered that water was composed of ***two atoms*** of hydrogen ***for each atom*** of oxygen. Therefore, in the above analysis, *in the 11.1 grams of hydrogen there were twice as many atoms as in the 88.9 grams of oxygen*. Therefore, an oxygen atom must weigh about 16 times as much as a hydrogen atom:

$$\frac{\frac{88.9\ g\ Oxygen}{1\ atom}}{\frac{111\ g\ Hydrogen}{2\ atoms}} = 16 \tag{2.4.3}$$

Hydrogen, the lightest element, was assigned a relative mass of '1', and the other elements were assigned 'atomic masses' relative to this value for hydrogen. Thus, oxygen was assigned an atomic mass of 16. We now know that a **hydrogen** atom has a mass of **1.6735 x 10^{-24}** grams, and that the **oxygen** atom has a mass of **2.6561 X 10^{-23}** grams. As we saw earlier, it is convenient to use a reference unit when dealing with such small numbers: the **atomic mass unit**. The atomic mass unit (***amu***) was not standardized against hydrogen, but rather, against the ^{12}C isotope of **carbon** (***amu* = 12**).

Thus, the mass of the **hydrogen atom** (^{1}H) is 1.0080 *amu*, and the mass of **an oxygen atom** (^{16}O) is 15.995 *amu*. Once the masses of atoms were determined, the ***amu*** could be assigned an actual value:

1 ***amu*** = 1.66054 x 10^{-24} **grams** conversely: 1 **gram** = 6.02214 x 10^{23} ***amu***

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Mass Numbers and Atomic Mass of Elements: Mass Numbers and Atomic Mass of Elements, YouTube(opens in new window)

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Average Atomic Mass

Although the masses of the electron, the proton, and the neutron are known to a high degree of precision (Table 2.3.1), the mass of any given atom is not simply the sum of the masses of its electrons, protons, and neutrons. For example, the ratio of the masses of ^{1}H (hydrogen) and ^{2}H (deuterium) is actually 0.500384, rather than 0.49979 as predicted from the numbers of neutrons and protons present. Although the difference in mass is small, it is extremely important because it is the source of the huge amounts of energy released in nuclear reactions.

Because atoms are much too small to measure individually and do not have charges, there is no convenient way to accurately measure absolute atomic masses. Scientists can measure relative atomic masses very accurately, however, using an instrument called a mass spectrometer. The technique is conceptually similar to the one Thomson used to determine the mass-to-charge ratio of the electron. First, electrons are removed from or added to atoms or molecules, thus producing charged particles called ions. When an electric field is applied, the ions are accelerated into a separate chamber where they are deflected from their initial trajectory by a magnetic field, like the electrons in Thomson's experiment. The extent of the deflection depends on the mass-to-charge ratio of the ion. By measuring the relative deflection of ions that have the same charge, scientists can determine their relative masses (Figure 2.4.1). Thus it is not possible to calculate absolute atomic masses accurately by simply adding together the masses of the electrons, the protons, and the neutrons, and absolute atomic masses cannot be measured, but relative masses can be measured very accurately. It is actually rather common in chemistry to encounter a quantity whose magnitude can be measured only relative to some other quantity, rather than absolutely. We will encounter many other examples later in this text. In such cases, chemists usually define a standard by arbitrarily assigning a numerical value to one of the quantities, which allows them to calculate numerical values for the rest.

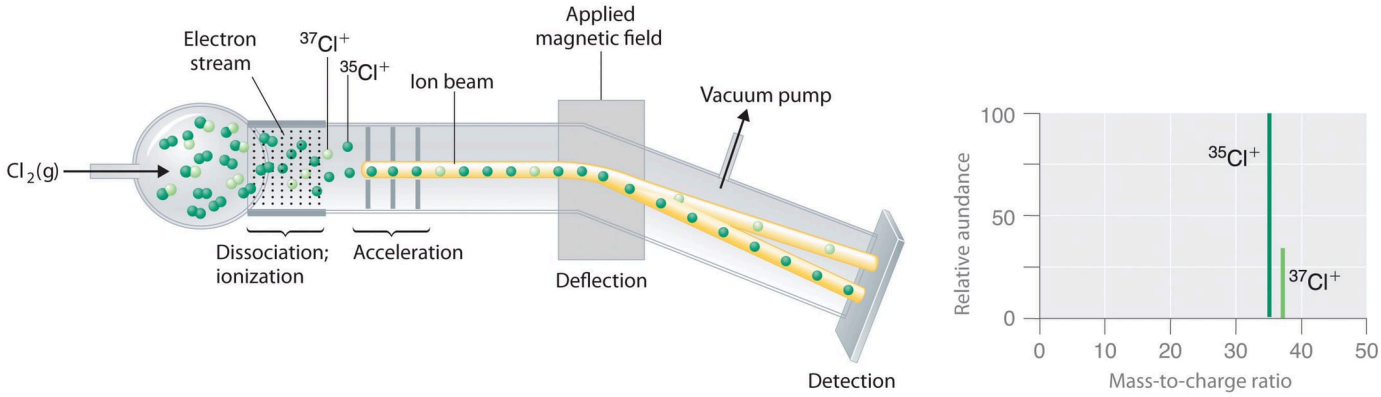


Figure 2.4.1: Determining Relative Atomic Masses Using a Mass Spectrometer. Chlorine consists of two isotopes, ^{35}Cl and ^{37}Cl, in approximately a 3:1 ratio. (a) When a sample of elemental chlorine is injected into the mass spectrometer, electrical energy is used to dissociate the Cl_2 molecules into chlorine atoms and convert the chlorine atoms to Cl^+ ions. The ions are then accelerated into a magnetic field. The extent to which the ions are deflected by the magnetic field depends on their relative mass-to-charge ratios. Note that the lighter $^{35}Cl^+$ ions are deflected more than the heavier $^{37}Cl^+$ ions. By measuring the relative deflections of the ions, chemists can determine their mass-to-charge ratios and thus their masses. (b) Each peak in the mass spectrum corresponds to an ion with a particular mass-to-charge ratio. The abundance of the two isotopes can be determined from the heights of the peaks.

A: Diagram of a mass spectrometer, showing analysis of gaseous chlorine. B: Mass spectrum of chlorine.

The arbitrary standard that has been established for describing atomic mass is the atomic mass unit (amu or u), defined as one-twelfth of the mass of one atom of ^{12}C. Because the masses of all other atoms are calculated relative to the ^{12}C standard, ^{12}C is the only atom listed in Table 2.3.2 whose exact atomic mass is equal to the mass number. Experiments have shown that 1 amu = 1.66×10^{-24} g.

Mass spectrometric experiments give a value of 0.167842 for the ratio of the mass of ^{2}H to the mass of ^{12}C, so the **absolute mass** of ^{2}H is

$$\frac{\text{mass of } {}^{2}\text{H}}{\text{mass of } {}^{12}\text{C}} \times \text{mass of } {}^{12}\text{C} = 0.167842 \times 12 \text{ amu} = 2.104104 \text{ amu} \tag{2.4.4}$$

The masses of the other elements are determined in a similar way.

The periodic table lists the atomic masses of all the elements. Comparing these values with those given for some of the isotopes in Table 2.3.2 reveals that the atomic masses given in the periodic table never correspond exactly to those of any of the isotopes. Because most elements exist as mixtures of several stable isotopes, the atomic mass of an element is defined as the weighted average of the masses of the isotopes. For example, naturally occurring carbon is largely a mixture of two isotopes: 98.89% ^{12}C (mass = 12 amu by definition) and 1.11% ^{13}C (mass = 13.003355 amu). The percent abundance of ^{14}C is so low that it can be ignored in this calculation. The average atomic mass of carbon is then calculated as follows:

$$(0.9889 \times 12 \text{ amu}) + (0.0111 \times 13.003355 \text{ amu}) = 12.01 \text{ amu} \tag{2.4.5}$$

Carbon is predominantly ^{12}C, so its average atomic mass should be close to 12 amu, which is in agreement with this calculation.

The value of 12.01 is shown under the symbol for C in the periodic table, although without the abbreviation amu, which is customarily omitted. Thus the tabulated atomic mass of carbon or any other element is the weighted average of the masses of the naturally occurring isotopes.

Example 2.4.1: Bromine

Naturally occurring bromine consists of the two isotopes listed in the following table:

Solutions to Example 2.4.1

Isotope	Exact Mass (amu)	Percent Abundance (%)
^{79}Br	78.9183	50.69
^{81}Br	80.9163	49.31

Calculate the atomic mass of bromine.

Given: exact mass and percent abundance

Asked for: atomic mass

Strategy:

A. Convert the percent abundances to decimal form to obtain the mass fraction of each isotope.
B. Multiply the exact mass of each isotope by its corresponding mass fraction (percent abundance ÷ 100) to obtain its weighted mass.
C. Add together the weighted masses to obtain the atomic mass of the element.
D. Check to make sure that your answer makes sense.

Solution:

A The atomic mass is the weighted average of the masses of the isotopes. In general, we can write

atomic mass of element = [(mass of isotope 1 in amu) (mass fraction of isotope 1)] + [(mass of isotope 2) (mass fraction of isotope 2)] + ...

Bromine has only two isotopes. Converting the percent abundances to mass fractions gives

$$^{79}\text{Br}: \frac{50.69}{100} = 0.5069$$

$$^{81}\text{Br}: \frac{49.31}{100} = 0.4931$$

B Multiplying the exact mass of each isotope by the corresponding mass fraction gives the isotope's weighted mass:

$$^{79}\text{Br} : 79.9183 \ \ amu \times 0.5069 = 40.00 \ \ amu$$

$$^{81}\text{Br} : 80.9163 \ \ amu \times 0.4931 = 39.90 \ \ amu$$

C The sum of the weighted masses is the atomic mass of bromine is

40.00 amu + 39.90 amu = 79.90 amu

D This value is about halfway between the masses of the two isotopes, which is expected because the percent abundance of each is approximately 50%.

Exercise 2.4.1

Magnesium has the three isotopes listed in the following table:

Solutions to Example 2.4.1

Isotope	Exact Mass (amu)	Percent Abundance (%)
^{24}Mg	23.98504	78.70
^{25}Mg	24.98584	10.13
^{26}Mg	25.98259	11.17

Use these data to calculate the atomic mass of magnesium.

Answer available at the end of this section.

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Finding the Averaged Atomic Weight of an Element: Finding the Averaged Atomic Weight of an Element(opens in new window) [youtu.be]

Summary

The mass of an atom is a weighted average that is largely determined by the number of its protons and neutrons, whereas the number of protons and electrons determines its charge. Each atom of an element contains the same number of protons, known as the atomic number (Z). Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called isotopes. Each isotope of a given element has the same atomic number but a different mass number (A), which is the sum of the numbers of protons and neutrons. The relative masses of atoms are reported using the atomic mass unit (amu), which is defined as one-twelfth of the mass of one atom of carbon-12, with 6 protons, 6 neutrons, and 6 electrons. The atomic mass of an element is the weighted average of the masses of the naturally occurring isotopes. When one or more electrons are added to or removed from an atom or molecule, a charged particle called an ion is produced, whose charge is indicated by a superscript after the symbol.

Answers

Exercise 2.4.1

24.31 amu

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2.5: The Periodic Table

Learning Objectives

- To become familiar with the organization of the periodic table.

Rutherford's nuclear model of the atom helped explain why atoms of different elements exhibit different chemical behavior. The identity of an element is defined by its *atomic number (Z)*, the number of protons in the nucleus of an atom of the element. The atomic number is therefore different for each element. The known elements are arranged in order of increasing Z in the *periodic table* (Figure 2.5.1). The rationale for the peculiar format of the periodic table is explained later. Each element is assigned a unique one-, two-, or three-letter symbol. The names of the elements are listed in the periodic table, along with their symbols, atomic numbers, and atomic masses. The chemistry of each element is determined by its number of protons and electrons. In a neutral atom, the number of electrons equals the number of protons.

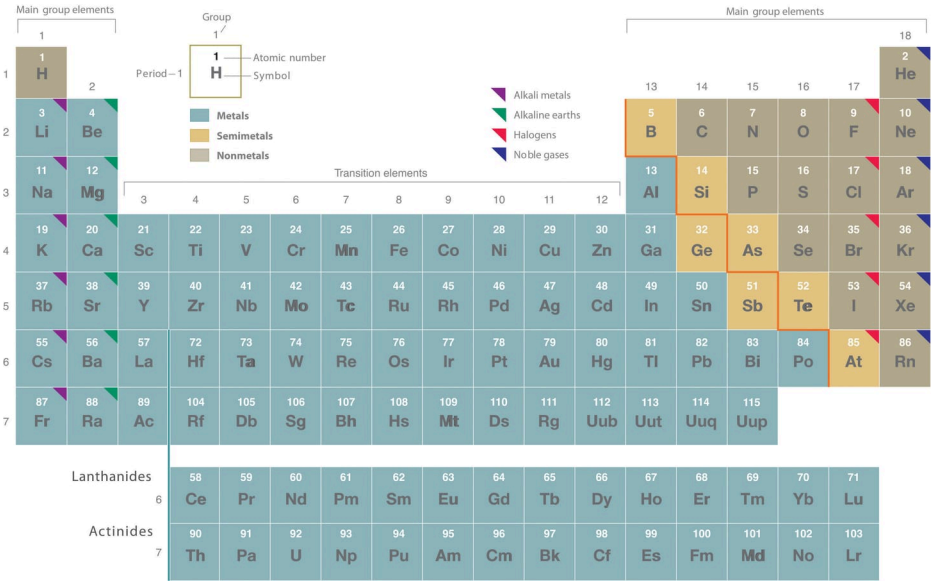


Figure 2.5.1: The Periodic Table Showing the Elements in Order of Increasing Z. The metals are on the bottom left in the periodic table, and the nonmetals are at the top right. The semimetals lie along a diagonal line separating the metals and nonmetals. An interactive Periodic table can be found Periodic Table of the Elements, LibreTexts. (CC-BY-SA-NC 3.0; Anonymous via LibreTexts)

The elements are arranged in a periodic table, which is probably the single most important learning aid in chemistry. It summarizes huge amounts of information about the elements in a way that facilitates the prediction of many of their properties and chemical reactions. The elements are arranged in seven horizontal rows, in order of increasing atomic number from left to right and top to bottom. The rows are called periods, and they are numbered from 1 to 7. The elements are stacked in such a way that elements with similar chemical properties form vertical columns, called groups, numbered from 1 to 18 (older periodic tables use a system based on roman numerals). Groups 1, 2, and 13–18 are the main group elements, listed as A in older tables. Groups 3–12 are in the middle of the periodic table and are the transition elements, listed as B in older tables. The two rows of 14 elements at the bottom of the periodic table are the lanthanides and the actinides, whose positions in the periodic table are indicated in group 3.

Metals, Nonmetals, and Semimetals

The heavy orange zigzag line running diagonally from the upper left to the lower right through groups 13–16 in Figure 2.5.1 divides the elements into metals (in blue, below and to the left of the line) and nonmetals (in bronze, above and to the right of the line). Gold-colored lements that lie along the diagonal line exhibit properties intermediate between metals and nonmetals; they are called semimetals.

The distinction between metals and nonmetals is one of the most fundamental in chemistry. Metals—such as copper or gold—are good conductors of electricity and heat; they can be pulled into wires because they are ductile; they can be hammered or pressed into thin sheets or foils because they are malleable; and most have a shiny appearance, so they are lustrous. The vast majority of the known elements are metals. Of the metals, only mercury is a liquid at room temperature and pressure; all the rest are solids.

Nonmetals, in contrast, are generally poor conductors of heat and electricity and are not lustrous. Nonmetals can be gases (such as chlorine), liquids (such as bromine), or solids (such as iodine) at room temperature and pressure. Most solid nonmetals are brittle, so they break into small pieces when hit with a hammer or pulled into a wire. As expected, semimetals exhibit properties intermediate between metals and nonmetals.

Example 2.5.1: Classifying Elements

Based on its position in the periodic table, do you expect selenium to be a metal, a nonmetal, or a semimetal?

Given: element

Asked for: classification

Strategy:

Find selenium in the periodic table shown in Figure 2.5.1 and then classify the element according to its location.

Solution:

The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 2.5.1, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

Exercise 2.5.1

Based on its location in the periodic table, do you expect indium to be a nonmetal, a metal, or a semimetal?

Answer available at the end of this section.

As previously noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins. For example, the elements of Group 1 are known as the alkali metals, Group 2 are the alkaline earth metals, Group 17 are the halogens, and Group 18 are the noble gases.

Group 1: The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal. The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively.

Group 2: The Alkaline Earth Metals

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium, strontium, and barium are rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.

Group 17: The Halogens

The halogens are fluorine, chlorine, bromine, iodine, and astatine. The name halogen is derived from the Greek words for “salt forming,” which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt).

Compounds that contain the fluoride ion are added to toothpaste and the water supply to prevent dental cavities. Fluorine is also found in Teflon coatings on kitchen utensils. Although chlorofluorocarbon propellants and refrigerants are believed to lead to the depletion of Earth’s ozone layer and contain both fluorine and chlorine, the latter is responsible for the adverse effect on the ozone layer. Bromine and iodine are less abundant than chlorine, and astatine is so radioactive that it exists in only negligible amounts in nature.

Group 18: The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, and radon. Because the noble gases are composed of only single atoms, they are called monatomic. At room temperature and pressure, they are unreactive gases. Because of their lack of reactivity, for many years they were called inert gases or rare gases. However, the first chemical compounds containing the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

> The noble gases are unreactive at room temperature and pressure.

Summary

The periodic table is used as a predictive tool. It arranges of the elements in order of increasing atomic number. Elements that exhibit similar chemistry appear in vertical columns called groups (numbered 1–18 from left to right); the seven horizontal rows are called periods. Some of the groups have widely-used common names, including the alkali metals (Group 1) and the alkaline earth metals (Group 2) on the far left, and the halogens (Group 17) and the noble gases (Group 18) on the far right. The elements can be broadly divided into metals, nonmetals, and semimetals. Semimetals exhibit properties intermediate between those of metals and nonmetals. Metals are located on the left of the periodic table, and nonmetals are located on the upper right. They are separated by a diagonal band of semimetals. Metals are lustrous, good conductors of electricity, and readily shaped (they are ductile and malleable), whereas solid nonmetals are generally brittle and poor electrical conductors. Other important groupings of elements in the periodic table are the main group elements, the transition metals, the lanthanides, and the actinides.

Answers

Exercise 2.5.1

metal

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2.6: Molecules and Molecular Compounds

Learning Objectives

- to understand the differences between covalent and ionic bonding.

The atoms in all substances that contain multiple atoms are held together by electrostatic interactions—interactions between electrically charged particles such as protons and electrons. Electrostatic attraction between oppositely charged species (positive and negative) results in a force that causes them to move toward each other, like the attraction between opposite poles of two magnets. In contrast, electrostatic repulsion between two species with the same charge (either both positive or both negative) results in a force that causes them to repel each other, as do the same poles of two magnets. Atoms form chemical compounds when the attractive electrostatic interactions between them are stronger than the repulsive interactions. Collectively, the attractive interactions between atoms are called chemical bonds.

Chemical bonds are generally divided into two fundamentally different types: ionic and covalent. In reality, however, the bonds in most substances are neither purely ionic nor purely covalent, but lie on a spectrum between these extremes. Although purely ionic and purely covalent bonds represent extreme cases that are seldom encountered in any but very simple substances, a brief discussion of these two extremes helps explain why substances with different kinds of chemical bonds have very different properties. Ionic compounds consist of positively and negatively charged ions held together by strong electrostatic forces, whereas covalent compounds generally consist of molecules, which are groups of atoms in which one or more pairs of electrons are shared between bonded atoms. In a covalent bond, atoms are held together by the electrostatic attraction between the positively charged nuclei of the bonded atoms and the negatively charged electrons they share. This discussion of structures and formulas begins by describing covalent compounds. The energetic factors involved in bond formation are described in more quantitative detail in later.

> Ionic compounds consist of ions of opposite charges held together by strong electrostatic forces, whereas pairs of electrons are shared between bonded atoms in covalent compounds.

Covalent Molecules and Compounds

Just as an atom is the simplest unit that has the fundamental chemical properties of an element, a molecule is the simplest unit that has the fundamental chemical properties of a covalent compound. Some pure elements exist as covalent molecules. Hydrogen, nitrogen, oxygen, and the halogens occur naturally as the diatomic (“two atoms”) molecules H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2 (part (a) in Figure $2.6.1$). Similarly, a few pure elements exist as polyatomic (“many atoms”) molecules, such as elemental phosphorus and sulfur, which occur as P_4 and S_8 (part (b) in Figure $2.6.1$).

Each covalent compound is represented by a molecular formula, which gives the atomic symbol for each component element, in a prescribed order, accompanied by a subscript indicating the number of atoms of that element in the molecule. The subscript is written only if the number of atoms is greater than 1. For example, water, with two hydrogen atoms and one oxygen atom per molecule, is written as H_2O. Similarly, carbon dioxide, which contains one carbon atom and two oxygen atoms in each molecule, is written as CO_2.

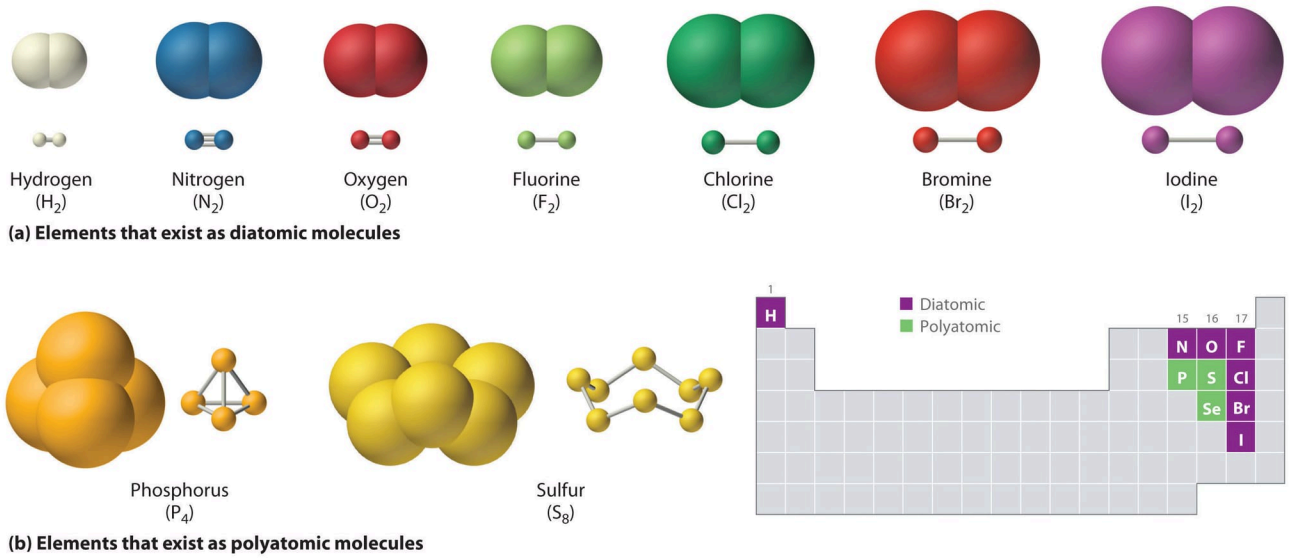


Figure 2.6.1: Elements That Exist as Covalent Molecules. (a) Several elements naturally exist as diatomic molecules, in which two atoms (E) are joined by one or more covalent bonds to form a molecule with the general formula E2. (b) A few elements naturally exist as polyatomic molecules, which contain more than two atoms. For example, phosphorus exists as P4 tetrahedra—regular polyhedra with four triangular sides—with a phosphorus atom at each vertex. Elemental sulfur consists of a puckered ring of eight sulfur atoms connected by single bonds. Selenium is not shown due to the complexity of its structure.

A: Elements that exist as diatomic molecules: H2, N2, O2, F2, Cl2, Br2, and I2. B: Elements that exist as polyatomic molecules: P4 and S8.

Covalent compounds that predominantly contain carbon and hydrogen are called organic compounds. The convention for representing the formulas of organic compounds is to write carbon first, followed by hydrogen and then any other elements in alphabetical order (e.g., CH_4O is methyl alcohol, a fuel). Compounds that consist primarily of elements other than carbon and hydrogen are called inorganic compounds; they include both covalent and ionic compounds. In inorganic compounds, the component elements are listed beginning with the one farthest to the left in the periodic table, as in CO_2 or SF_6. Those in the same group are listed beginning with the lower element and working up, as in ClF. By convention, however, when an inorganic compound contains both hydrogen and an element from groups 13–15, hydrogen is usually listed last in the formula. Examples are ammonia (NH_3) and silane (SiH_4). Compounds such as water, whose compositions were established long before this convention was adopted, are always written with hydrogen first: Water is always written as H_2O, not OH_2. The conventions for inorganic acids, such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4), are described in Section 2.8.

For organic compounds: write C first, then H, and then the other elements in alphabetical order. For molecular inorganic compounds: start with the element at far left in the periodic table; list elements in same group beginning with the lower element and working up.

Example 2.6.1

Write the molecular formula of each compound.

a. The phosphorus-sulfur compound that is responsible for the ignition of so-called strike anywhere matches has 4 phosphorus atoms and 3 sulfur atoms per molecule.
b. Ethyl alcohol, the alcohol of alcoholic beverages, has 1 oxygen atom, 2 carbon atoms, and 6 hydrogen atoms per molecule.
c. Freon-11, once widely used in automobile air conditioners and implicated in damage to the ozone layer, has 1 carbon atom, 3 chlorine atoms, and 1 fluorine atom per molecule.

Given: identity of elements present and number of atoms of each

Asked for: molecular formula

Strategy:

A. Identify the symbol for each element in the molecule. Then identify the substance as either an organic compound or an inorganic compound.
B. If the substance is an organic compound, arrange the elements in order beginning with carbon and hydrogen and then list the other elements alphabetically. If it is an inorganic compound, list the elements beginning with the one farthest left in the periodic table. List elements in the same group starting with the lower element and working up.
C. From the information given, add a subscript for each kind of atom to write the molecular formula.

Solution

a

A. The molecule has 4 phosphorus atoms and 3 sulfur atoms. Because the compound does not contain mostly carbon and hydrogen, it is inorganic.
B. Phosphorus is in group 15, and sulfur is in group 16. Because phosphorus is to the left of sulfur, it is written first.
C. Writing the number of each kind of atom as a right-hand subscript gives P_4S_3 as the molecular formula.

b.

A. Ethyl alcohol contains predominantly carbon and hydrogen, so it is an organic compound.
B. The formula for an organic compound is written with the number of carbon atoms first, the number of hydrogen atoms next, and the other atoms in alphabetical order: CHO.
C. Adding subscripts gives the molecular formula]C_2H_6O.

c

A. Freon-11 contains carbon, chlorine, and fluorine. It can be viewed as either an inorganic compound or an organic compound (in which fluorine has replaced hydrogen). The formula for Freon-11 can therefore be written using either of the two conventions.
B. According to the convention for inorganic compounds, carbon is written first because it is farther left in the periodic table. Fluorine and chlorine are in the same group, so they are listed beginning with the lower element and working up: CClF. Adding subscripts gives the molecular formula CCl_3F.
C. We obtain the same formula for Freon-11 using the convention for organic compounds. The number of carbon atoms is written first, followed by the number of hydrogen atoms (zero) and then the other elements in alphabetical order, also giving CCl_3F.

Exercise 2.6.1

Write the molecular formula for each compound.

a. Nitrous oxide, also called “laughing gas,” has 2 nitrogen atoms and 1 oxygen atom per molecule. Nitrous oxide is used as a mild anesthetic for minor surgery and as the propellant in cans of whipped cream.
b. Sucrose, also known as cane sugar, has 12 carbon atoms, 11 oxygen atoms, and 22 hydrogen atoms.
c. Sulfur hexafluoride, a gas used to pressurize “unpressurized” tennis balls and as a coolant in nuclear reactors, has 6 fluorine atoms and 1 sulfur atom per molecule.

Answer a available at the end of this section.

Representations of Molecular Structures

Molecular formulas give only the elemental composition of molecules. In contrast, structural formulas show which atoms are bonded to one another and, in some cases, the approximate arrangement of the atoms in space. Knowing the structural formula of a compound enables chemists to create a three-dimensional model, which provides information about how that compound will behave physically and chemically.

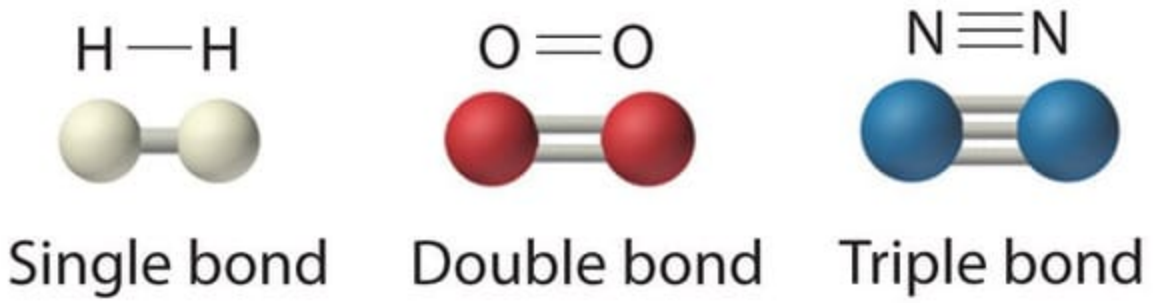


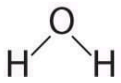
Figure 2.6.2: Molecules That Contain Single, Double, and Triple Bonds. Hydrogen (H_2) has a single bond between atoms. Oxygen (O_2) has a double bond between atoms, indicated by two lines (=). Nitrogen (N_2) has a triple bond between atoms, indicated by three lines (≡). Each bond represents an electron pair.

The structural formula for H_2 can be drawn as H–H and that for I_2 as I–I, where the line indicates a single pair of shared electrons, a single bond. Two pairs of electrons are shared in a double bond, which is indicated by two lines—for example, O_2 is O=O. Three electron pairs are shared in a triple bond, which is indicated by three lines—for example, N_2 is N≡N (see Figure 2.6.2). Carbon is unique in the extent to which it forms single, double, and triple bonds to itself and other elements. The number of bonds formed by an atom in its covalent compounds is not arbitrary. Hydrogen, oxygen, nitrogen, and carbon have very strong tendencies to form substances in which they have one, two, three, and four bonds to other atoms, respectively (Table 2.6.1).

Table 2.6.1: The Number of Bonds That Selected Atoms Commonly Form to Other Atoms

Atom	Number of Bonds
H (group 1)	1
O (group 16)	2
N (group 15)	3
C (group 14)	4

The structural formula for water can be drawn as follows:



Because the latter approximates the experimentally determined shape of the water molecule, it is more informative. Similarly, ammonia (NH_3) and methane (CH_4) are often written as planar molecules:

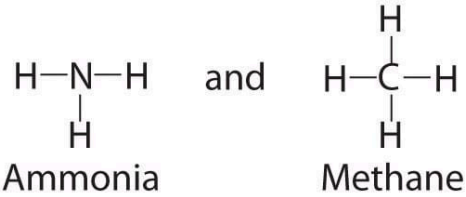


Figure 2.6.3, is tetrahedral: the hydrogen atoms are positioned at every other vertex of a cube. Many compounds—carbon compounds, in particular—have four bonded atoms arranged around a central atom to form a tetrahedron.

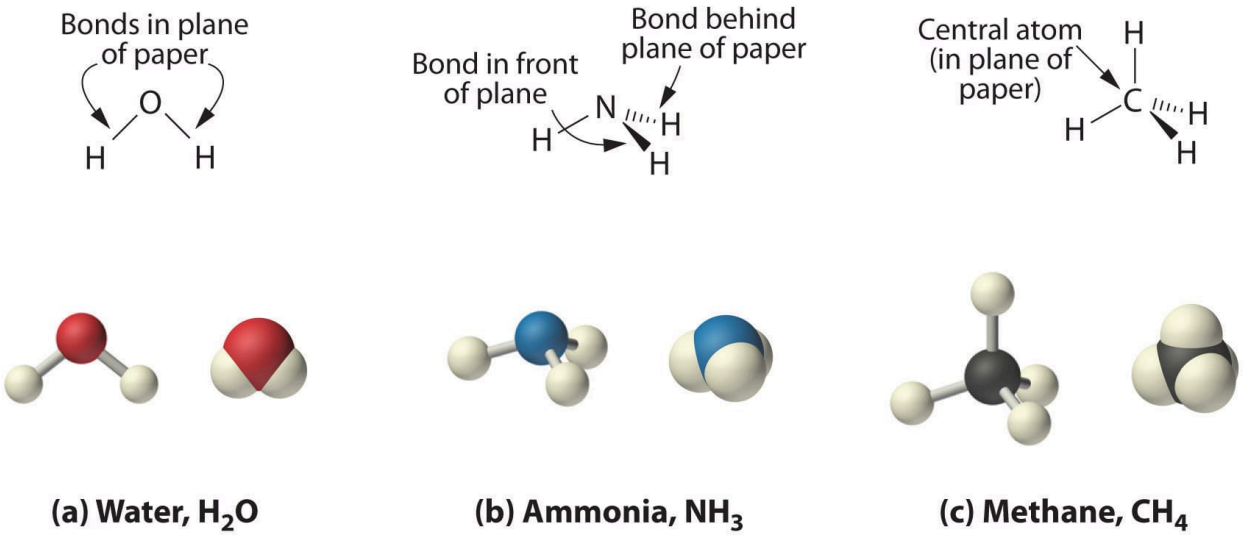
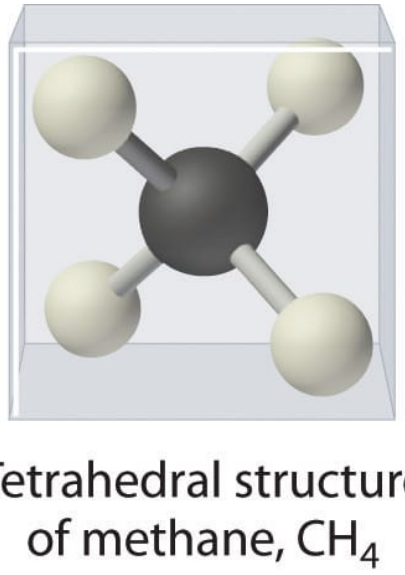


Figure 2.6.3: The Three-Dimensional Structures of Water, Ammonia, and Methane. (a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.

A: Bent configuration of H 2 O. B: Trigonal pyramidal configuration of ammonia. C: Tetrahedral configuration of methane.



Tetrahedral structure of methane, CH_4

Methane CH_4 has a three-dimensional, tetrahedral structure.

Figures 2.6.1, 2.6.2, and 2.6.3 illustrate different ways to represent the structures of molecules. It should be clear that there is no single “best” way to draw the structure of a molecule; the method used depends on which aspect of the structure should be emphasized and how much time and effort is required. Figure 2.6.4 shows some of the different ways to portray the structure of a slightly more complex molecule: methanol. These representations differ greatly in their information content. For example, the molecular formula for methanol (Figure 2.6.4*a*) gives only the number of each kind of atom; writing methanol as CH_4O tells nothing about its structure. In contrast, the structural formula (Figure 2.6.4*b*) indicates how the atoms are connected, but it makes methanol look as if it is planar (which it is not). Both the ball-and-stick model (part (c) in Figure 2.6.4) and the perspective drawing (Figure 2.6.4*d*) show the three-dimensional structure of the molecule. The latter (also called a wedge-and-dash representation) is the easiest way to sketch the structure of a molecule in three dimensions. It shows which atoms are above and below the plane of the paper by using wedges and dashes, respectively; the central atom is always assumed to be in the plane of the paper. The space-filling model (part (e) in Figure 2.6.4) illustrates the approximate relative sizes of the atoms in the molecule, but it does not show the bonds between the atoms. In addition, in a space-filling model, atoms at the “front” of the molecule may obscure atoms at the “back.”

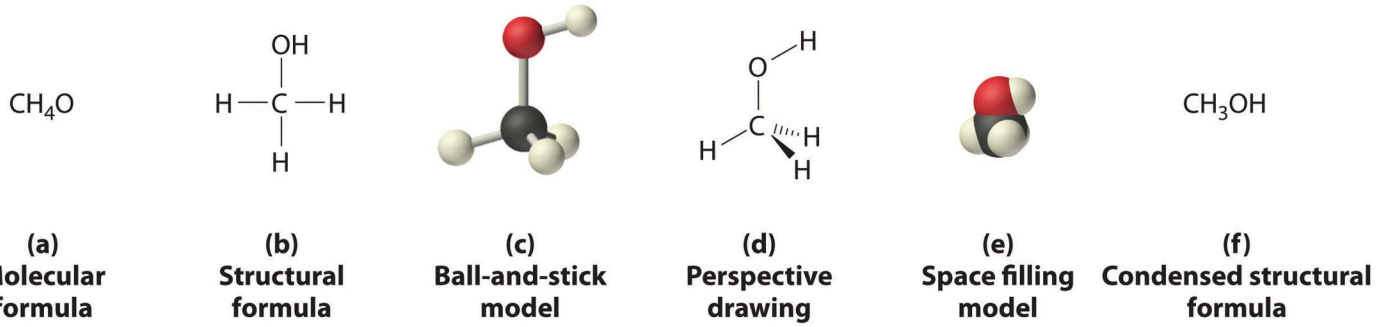


Figure 2.6.4: Different Ways of Representing the Structure of a Molecule. (a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a wedge-and-dash representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule.

Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a condensed structural formula (part (f) in Figure 2.6.4), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is CH_3OH, which indicates that the molecule contains a CH_3 unit that looks like a fragment of methane (CH_4). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an –OH group or as a water molecule in which one hydrogen atom has been replaced by a $–CH_3$ fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

Example 2.6.2: Molecular Formulas

Write the molecular formula for each compound. The condensed structural formula is given.

a. Sulfur monochloride (also called disulfur dichloride) is a vile-smelling, corrosive yellow liquid used in the production of synthetic rubber. Its condensed structural formula is ClSSCl.
b. Ethylene glycol is the major ingredient in antifreeze. Its condensed structural formula is $HOCH_2CH_2OH$.
c. Trimethylamine is one of the substances responsible for the smell of spoiled fish. Its condensed structural formula is $(CH_3)_3N$.

Given: condensed structural formula

Asked for: molecular formula

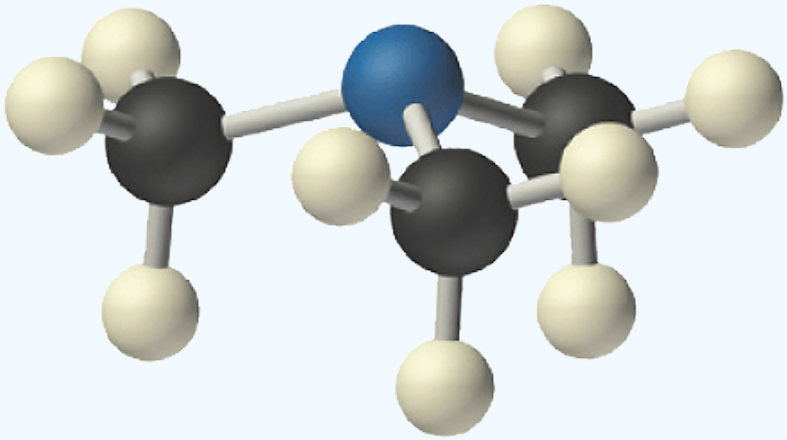
Strategy:

A. Identify every element in the condensed structural formula and then determine whether the compound is organic or inorganic.
B. As appropriate, use either organic or inorganic convention to list the elements. Then add appropriate subscripts to indicate the number of atoms of each element present in the molecular formula.

Solution:

The molecular formula lists the elements in the molecule and the number of atoms of each.

a. **A** Each molecule of sulfur monochloride has two sulfur atoms and two chlorine atoms. Because it does not contain mostly carbon and hydrogen, it is an inorganic compound. **B** Sulfur lies to the left of chlorine in the periodic table, so it is written first in the formula. Adding subscripts gives the molecular formula S_2Cl_2.
b. **A** Counting the atoms in ethylene glycol, we get six hydrogen atoms, two carbon atoms, and two oxygen atoms per molecule. The compound consists mostly of carbon and hydrogen atoms, so it is organic. **B** As with all organic compounds, C and H are written first in the molecular formula. Adding appropriate subscripts gives the molecular formula $C_2H_6O_2$.
c. **A** The condensed structural formula shows that trimethylamine contains three CH_3 units, so we have one nitrogen atom, three carbon atoms, and nine hydrogen atoms per molecule. Because trimethylamine contains mostly carbon and hydrogen, it is an organic compound. **B** According to the convention for organic compounds, C and H are written first, giving the molecular formula C_3H_9N.

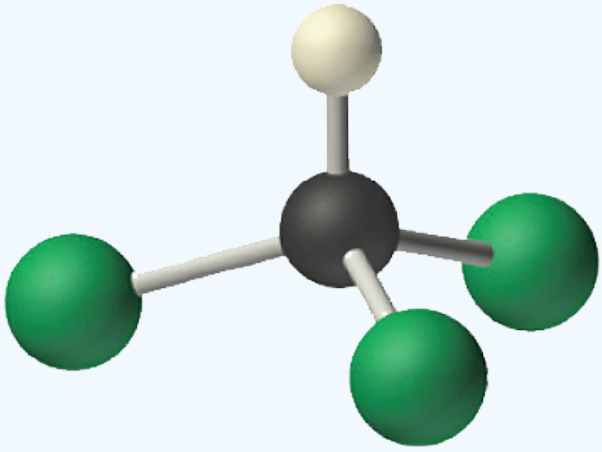


Trimethylamine

Exercise 2.6.2: Molecular Formulas

Write the molecular formula for each molecule.

a. Chloroform, which was one of the first anesthetics and was used in many cough syrups until recently, contains one carbon atom, one hydrogen atom, and three chlorine atoms. Its condensed structural formula is $\mathrm{CHCl_3}$.
b. Hydrazine is used as a propellant in the attitude jets of the space shuttle. Its condensed structural formula is $\mathrm{H_2NNH_2}$.
c. Putrescine is a pungent-smelling compound first isolated from extracts of rotting meat. Its condensed structural formula is H2NCH2CH2CH2CH2NH2. This is often written as $\mathrm{H_2N(CH_2)_4NH_2}$ to indicate that there are four CH2 fragments linked together.



Chloroform

Answer a available at the end of this section.

Summary

There are two fundamentally different kinds of chemical bonds (covalent and ionic) that cause substances to have very different properties. The atoms in chemical compounds are held together by attractive electrostatic interactions known as chemical bonds. The molecular formula of a covalent compound gives the types and numbers of atoms present. Compounds that contain predominantly carbon and hydrogen are called organic compounds, whereas compounds that consist primarily of elements other than carbon and hydrogen are inorganic compounds. Diatomic molecules contain two atoms, and polyatomic molecules contain more than two. A structural formula indicates the composition and approximate structure and shape of a molecule. Covalent molecular compounds, in contrast, consist of discrete molecules held together by weak intermolecular forces and can be gases, liquids, or solids at room temperature and pressure.

Answers

Exercise 2.6.1

N_2O

$C_{12}H_{22}O_{11}$

SF_6

Exercise 2.6.2**: Molecular Formulas**

$CHCl_3$

N_2H_4

$C_4H_{12}N_2$

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2.7: Ions and Ionic Compounds

Learning Objectives

- Explain the bonding nature of ionic compounds.
- Relating microscopic bonding properties to macroscopic solid properties.

The substances described in the preceding discussion are composed of molecules that are electrically neutral; that is, the number of positively-charged protons in the nucleus is equal to the number of negatively-charged electrons. In contrast, ions are atoms or assemblies of atoms that have a net electrical charge. Ions that contain fewer electrons than protons have a net positive charge and are called cations. Conversely, ions that contain more electrons than protons have a net negative charge and are called anions. Ionic compounds contain both cations and anions in a ratio that results in no net electrical charge.

In covalent compounds, electrons are shared between bonded atoms and are simultaneously attracted to more than one nucleus. In contrast, ionic compounds contain cations and anions rather than discrete neutral molecules. Ionic compounds are held together by the attractive electrostatic interactions between cations and anions. In an ionic compound, the cations and anions are arranged in space to form an extended three-dimensional array that maximizes the number of attractive electrostatic interactions and minimizes the number of repulsive electrostatic interactions (Figure 2.7.1). As shown in Equation 2.7.1, the electrostatic energy of the interaction between two charged particles is proportional to the product of the charges on the particles and inversely proportional to the distance between them:

$$\text{electrostatic energy} \propto \frac{Q_1 Q_2}{r} \tag{2.7.1}$$

where Q_1 and Q_2 are the electrical charges on particles 1 and 2, and r is the distance between them. When Q_1 and Q_2 are both positive, corresponding to the charges on cations, the cations repel each other and the electrostatic energy is positive. When Q_1 and Q_2 are both negative, corresponding to the charges on anions, the anions repel each other and the electrostatic energy is again positive. The electrostatic energy is negative only when the charges have opposite signs; that is, positively charged species are attracted to negatively charged species and vice versa.

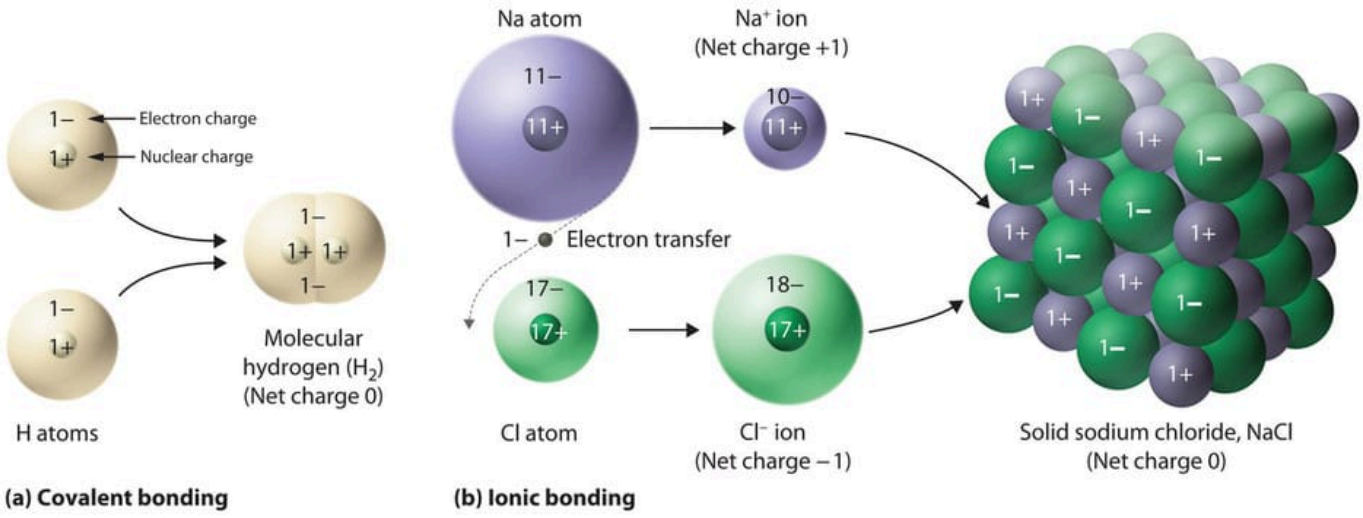


Figure 2.7.1: Covalent and Ionic Bonding. (a) In molecular hydrogen (H_2), two hydrogen atoms share two electrons to form a covalent bond. (b) The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting Na^+ and Cl^- ions form a three-dimensional solid that is held together by attractive electrostatic interactions.

A: Covalent bonding between two H atoms. B: Ionic bonding between sodium and chlorine, forming a lattice structure.

Ionic compounds contain both cations and anions in a ratio that results in zero electrical charge.

As shown in Figure 2.7.2, the strength of the interaction is proportional to the magnitude of the charges and decreases as the distance between the particles increases. These energetic factors are discussed in greater quantitative detail later.

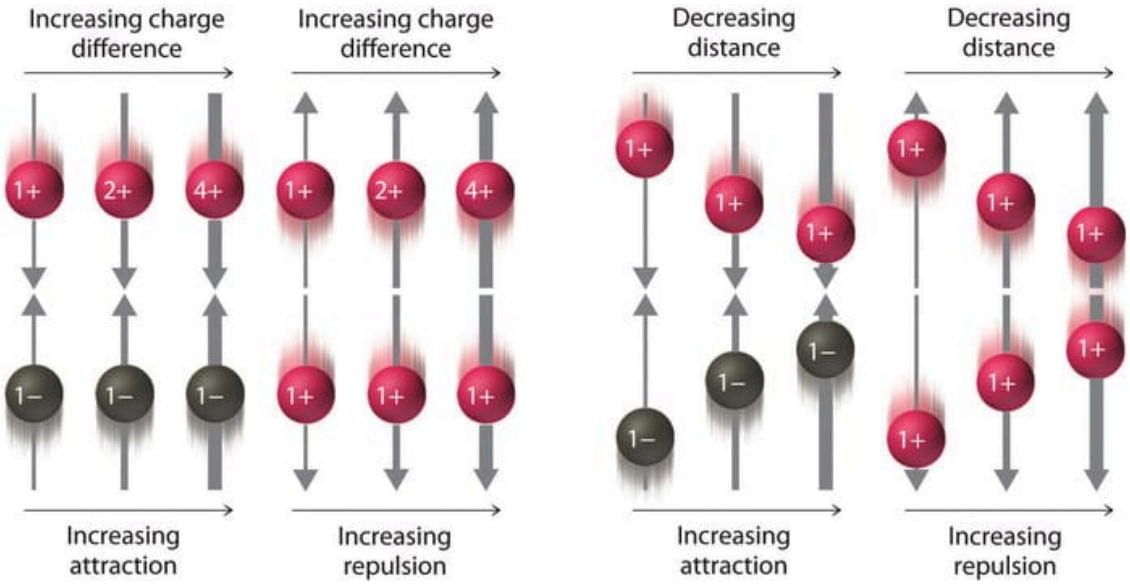


Figure 2.7.2: The Effect of Charge and Distance on the Strength of Electrostatic Interactions. As the charge on ions increases or the distance between ions decreases, so does the strength of the attractive (–...+) or repulsive (–...– or +...+) interactions. The strength of these interactions is represented by the thickness of the arrows.

> If the electrostatic energy is positive, the particles repel each other; if the electrostatic energy is negative, the particles are attracted to each other.

One example of an ionic compound is sodium chloride (NaCl; Figure 2.7.3), formed from sodium and chlorine. In forming chemical compounds, many elements have a tendency to gain or lose enough electrons to attain the same number of electrons as the noble gas closest to them in the periodic table. When sodium and chlorine come into contact, each sodium atom gives up an electron to become a Na^+ ion, with 11 protons in its nucleus but only 10 electrons (like neon), and each chlorine atom gains an electron to become a Cl^- ion, with 17 protons in its nucleus and 18 electrons (like argon), as shown in part (b) in Figure 2.7.1. Solid sodium chloride contains equal numbers of cations (Na^+) and anions (Cl^-), thus maintaining electrical neutrality. Each Na^+ ion is surrounded by 6 Cl^- ions, and each Cl^- ion is surrounded by 6 Na^+ ions. Because of the large number of attractive Na^+Cl^- interactions, the total attractive electrostatic energy in NaCl is great.

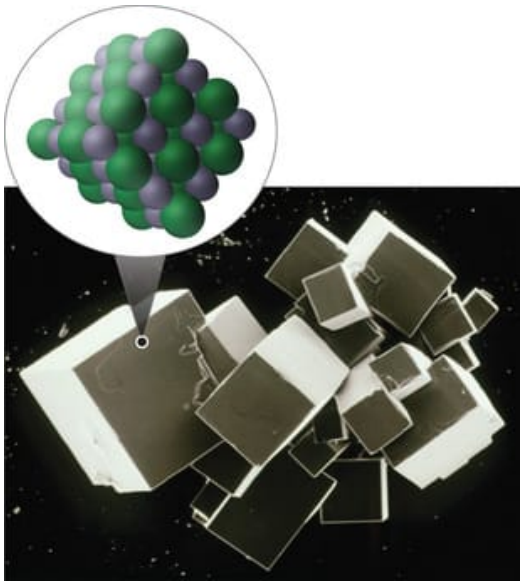


Figure 2.7.3: Sodium Chloride: an Ionic Solid. The planes of an NaCl crystal reflect the regular three-dimensional arrangement of its Na+ (purple) and Cl– (green) ions.

Consistent with a tendency to have the same number of electrons as the nearest noble gas, when forming ions, elements in groups 1, 2, and 3 tend to lose one, two, and three electrons, respectively, to form cations, such as Na^+ and Mg^{2+}. They then have the same number of electrons as the nearest noble gas: neon. Similarly, K^+, Ca^{2+}, and Sc^{3+} have 18 electrons each, like the nearest noble gas: argon. In addition, the elements in group 13 lose three electrons to form cations, such as Al^{3+}, again attaining the same number of electrons as the noble gas closest to them in the periodic table. Because the lanthanides and actinides formally belong to group 3, the most common ion formed by these elements is M^{3+}, where M represents the metal. Conversely, elements in groups 17, 16, and 15 often react to gain one, two, and three electrons, respectively, to form ions such as $Cl^–$, $S^{2–}$, and $P^{3–}$. Ions such as these, which contain only a single atom, are called monatomic ions. The charges of most monatomic ions derived from the main group elements can be predicted by simply looking at the periodic table and counting how many columns an element lies from the extreme left or right. For example, barium (in Group 2) forms Ba^{2+} to have the same number of electrons as its nearest noble gas, xenon; oxygen (in Group 16) forms $O^{2–}$ to have the same number of electrons as neon; and cesium (in Group 1) forms Cs^+, which has the same number of electrons as xenon. Note that this method is ineffective for most of the transition metals. Some common monatomic ions are listed in Table 2.7.1.

Elements in Groups 1, 2, and 3 tend to form 1+, 2+, and 3+ ions, respectively; elements in Groups 15, 16, and 17 tend to form 3–, 2–, and 1– ions, respectively.

Table 2.7.1: Some Common Monatomic Ions and Their Names

Group 1	Group 2	Group 3	Group 13	Group 15	Group 16	Group 17
Li^+ lithium	Be^{2+} beryllium			$N^{3–}$ nitride (azide)	$O^{2–}$ oxide	$F^–$ fluoride
Na^+ sodium	Mg^{2+} magnesium		Al^{3+} aluminum	$P^{3–}$ phosphide	$S^{2–}$ sulfide	$Cl^–$ chloride
K^+ potassium	Ca^{2+} calcium	Sc^{3+} scandium	Ga^{3+} gallium	$As^{3–}$ arsenide	$Se^{2–}$ selenide	$Br^–$ bromide
Rb^+ rubidium	Sr^{2+} strontium	Y^{3+} yttrium	In^{3+} indium		$Te^{2–}$ telluride	$I^–$ iodide
Cs^+ cesium	Ba^{2+} barium	La^{3+} lanthanum				

Example 2.7.1

Predict the charge on the most common monatomic ion formed by each element.

a. aluminum, used in the quantum logic clock, the world's most precise clock
b. selenium, used to make ruby-colored glass
c. yttrium, used to make high-performance spark plugs

Given: element

Asked for: ionic charge

Strategy:

A. Identify the group in the periodic table to which the element belongs. Based on its location in the periodic table, decide whether the element is a metal, which tends to lose electrons; a nonmetal, which tends to gain electrons; or a semimetal, which can do either.
B. After locating the noble gas that is closest to the element, determine the number of electrons the element must gain or lose to have the same number of electrons as the nearest noble gas.

Solution:

a. **A** Aluminum is a metal in group 13; consequently, it will tend to lose electrons. **B** The nearest noble gas to aluminum is neon. Aluminum will lose three electrons to form the Al^{3+} ion, which has the same number of electrons as neon.
b. **A** Selenium is a nonmetal in group 16, so it will tend to gain electrons. **B** The nearest noble gas is krypton, so we predict that selenium will gain two electrons to form the Se^{2-} ion, which has the same number of electrons as krypton.
c. **A** Yttrium is in group 3, and elements in this group are metals that tend to lose electrons. **B** The nearest noble gas to yttrium is krypton, so yttrium is predicted to lose three electrons to form Y^{3+}, which has the same number of electrons as krypton.

Exercise 2.7.1

Predict the charge on the most common monatomic ion formed by each element.

a. calcium, used to prevent osteoporosis
b. iodine, required for the synthesis of thyroid hormones
c. zirconium, widely used in nuclear reactors

Answer a available at the end of this section.

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Physical Properties of Ionic and Covalent Compounds

In general, ionic and covalent compounds have different physical properties. Ionic compounds form hard crystalline solids that melt at high temperatures and are resistant to evaporation. These properties stem from the characteristic internal structure of an ionic solid, illustrated schematically in Figure 2.7.4*a* which shows the three-dimensional array of alternating positive and negative ions held together by strong electrostatic attractions. In contrast, as shown in Figure 2.7.4*b* most covalent compounds consist of discrete molecules held together by comparatively weak intermolecular forces (the forces between molecules), even though the

atoms within each molecule are held together by strong intramolecular covalent bonds (the forces within the molecule).

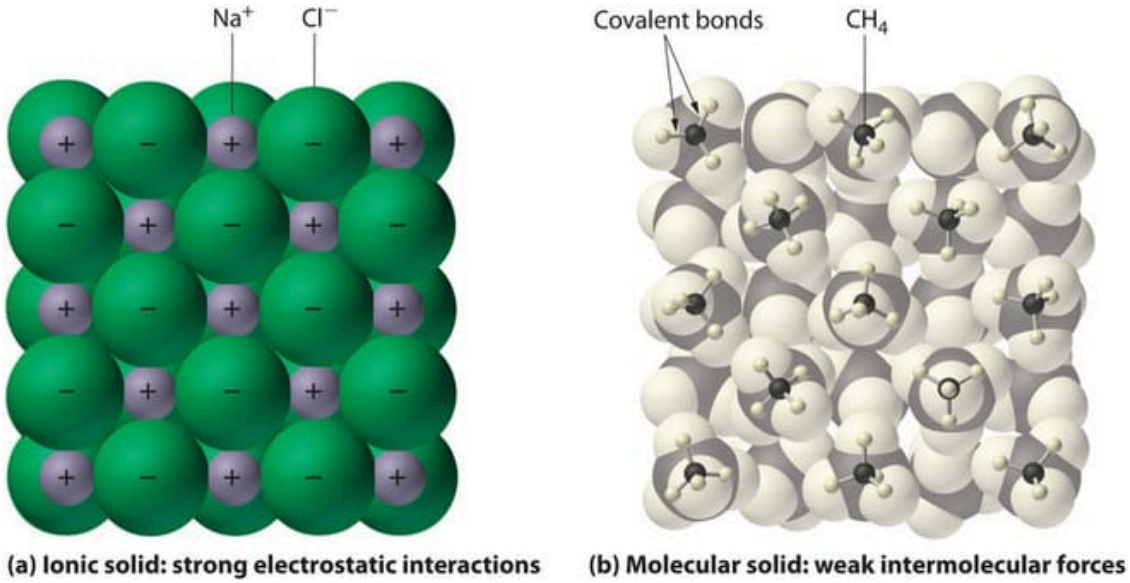


Figure 2.7.4: Interactions in Ionic and Covalent Solids. (a) The positively and negatively charged ions in an ionic solid such as sodium chloride (NaCl) are held together by strong electrostatic interactions. (b) In this representation of the packing of methane (CH_4) molecules in solid methane, a prototypical molecular solid, the methane molecules are held together in the solid only by relatively weak intermolecular forces, even though the atoms within each methane molecule are held together by strong covalent bonds.

A: Ionic solid of sodium and chloride ions, showing strong electrostatic interactions. B: Molecular solid consisting of methane, showing weak intermolecular forces.

Covalent substances can be gases, liquids, or solids at room temperature and pressure, depending on the strength of the intermolecular interactions. Covalent molecular solids tend to form soft crystals that melt at low temperatures and evaporate easily. Some covalent substances, however, are not molecular but consist of infinite three-dimensional arrays of covalently bonded atoms and include some of the hardest materials known, such as diamond. This topic will be addressed elsewhere. The covalent bonds that hold the atoms together in the molecules are unaffected when covalent substances melt or evaporate, so a liquid or vapor of independent molecules is formed. For example, at room temperature, methane, the major constituent of natural gas, is a gas that is composed of discrete $\mathrm{CH_4}$ molecules. A comparison of the different physical properties of ionic compounds and covalent molecular substances is given in Table 2.7.2.

Table 2.7.2: The Physical Properties of Typical Ionic Compounds and Covalent Molecular Substances

Ionic Compounds	Covalent Molecular Substances
hard solids	gases, liquids, or soft solids
high melting points	low melting points
nonvolatile	volatile

Summary

The atoms in chemical compounds are held together by attractive electrostatic interactions known as chemical bonds. Ionic compounds contain positively and negatively charged ions in a ratio that results in an overall charge of zero. The ions are held together in a regular spatial arrangement by electrostatic forces. Atoms or groups of atoms that possess a net electrical charge are called ions; they can have either a positive charge (cations) or a negative charge (anions). Ions can consist of one atom (monatomic ions) or several (polyatomic ions). The charges on monatomic ions of most main group elements can be predicted from the location of the element in the periodic table. Ionic compounds usually form hard crystalline solids with high melting points.

Answers

Exercise 2.7.1

Ca^{2+}

I^{-}

Zr^{4+}

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2.8: Naming Inorganic Compounds

Learning Objectives

- To describe the composition of a chemical compound.
- To name covalent compounds that contain up to three elements.

As with ionic compounds, the system for naming covalent compounds enables chemists to write the molecular formula from the name and vice versa. This and the following section describe the rules for naming simple covalent compounds, beginning with inorganic compounds and then turning to simple organic compounds that contain only carbon and hydrogen.

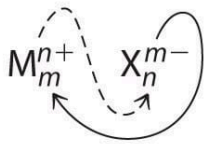
When chemists synthesize a new compound, they may not yet know its molecular or structural formula. In such cases, they usually begin by determining its empirical formula, the relative numbers of atoms of the elements in a compound, reduced to the smallest whole numbers. Because the empirical formula is based on experimental measurements of the numbers of atoms in a sample of the compound, it shows only the ratios of the numbers of the elements present. The difference between empirical and molecular formulas can be illustrated with butane, a covalent compound used as the fuel in disposable lighters. The molecular formula for butane is $\mathrm{C_4H_{10}}$. The ratio of carbon atoms to hydrogen atoms in butane is 4:10, which can be reduced to 2:5. The empirical formula for butane is therefore $\mathrm{C_2H_5}$. The formula unit is the absolute grouping of atoms or ions represented by the empirical formula of a compound, either ionic or covalent. Butane has the empirical formula $\mathrm{C_2H_5}$, but it contains two $\mathrm{C_2H_5}$ formula units, giving a molecular formula of $\mathrm{C_4H_{10}}$.

Because ionic compounds **do not** contain discrete molecules, empirical formulas are used to indicate their compositions. All compounds, whether ionic or covalent, must be electrically neutral. Consequently, the positive and negative charges in a formula unit must exactly cancel each other. If the cation and the anion have charges of equal magnitude, such as $\mathrm{Na^+}$ and $\mathrm{Cl^-}$, then the compound must have a 1:1 ratio of cations to anions, and the empirical formula must be NaCl. If the charges are not the same magnitude, then a cation:anion ratio other than 1:1 is needed to produce a neutral compound. In the case of $\mathrm{Mg^{2+}}$ and $\mathrm{Cl^-}$, for example, two $\mathrm{Cl^-}$ ions are needed to balance the two positive charges on each $\mathrm{Mg^{2+}}$ ion, giving an empirical formula of $\mathrm{MgCl_2}$. Similarly, the formula for the ionic compound that contains $\mathrm{Na^+}$ and $\mathrm{O^{2-}}$ ions is $\mathrm{Na_2O}$.

> Ionic compounds do not contain discrete molecules, so empirical formulas are used to indicate their compositions.

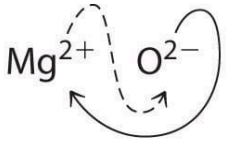
Binary Ionic Compounds

An ionic compound that contains only two elements, one present as a cation and one as an anion, is called a binary ionic compound. One example is $\mathrm{MgCl_2}$, a coagulant used in the preparation of tofu from soybeans. For binary ionic compounds, the subscripts in the empirical formula can also be obtained by crossing charges: use the absolute value of the charge on one ion as the subscript for the other ion. This method is shown schematically as follows:



Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

When crossing charges, it is sometimes necessary to reduce the subscripts to their simplest ratio to write the empirical formula. Consider, for example, the compound formed by $\mathrm{Mg^{2+}}$ and $\mathrm{O^{2-}}$. Using the absolute values of the charges on the ions as subscripts gives the formula $\mathrm{Mg_2O_2}$:



This simplifies to its correct empirical formula MgO. The empirical formula has one Mg^{2+} ion and one O^{2-} ion.

Example 2.8.1: Binary Ionic Compounds

Write the empirical formula for the simplest binary ionic compound formed from each ion or element pair.

a. Ga^{3+} and As^{3-}
b. Eu^{3+} and O^{2-}
c. calcium and chlorine

Given: ions or elements

Asked for: empirical formula for binary ionic compound

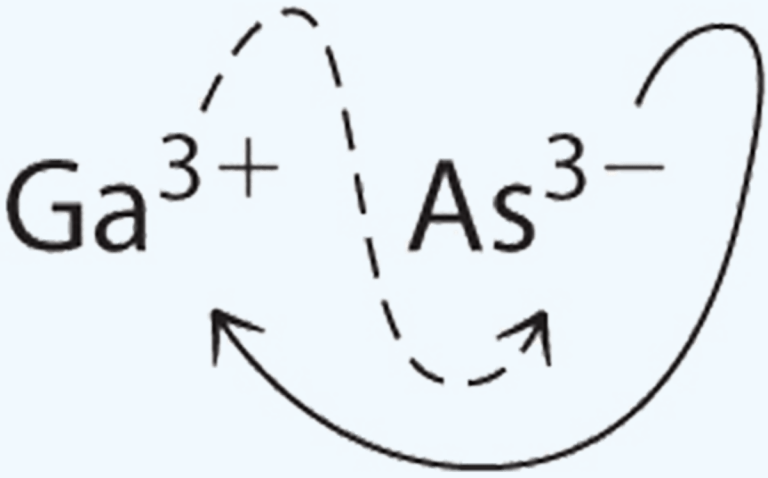
Strategy:

A. If not given, determine the ionic charges based on the location of the elements in the periodic table.
B. Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the lowest numbers

to write the empirical formula. Check to make sure the empirical formula is electrically neutral.

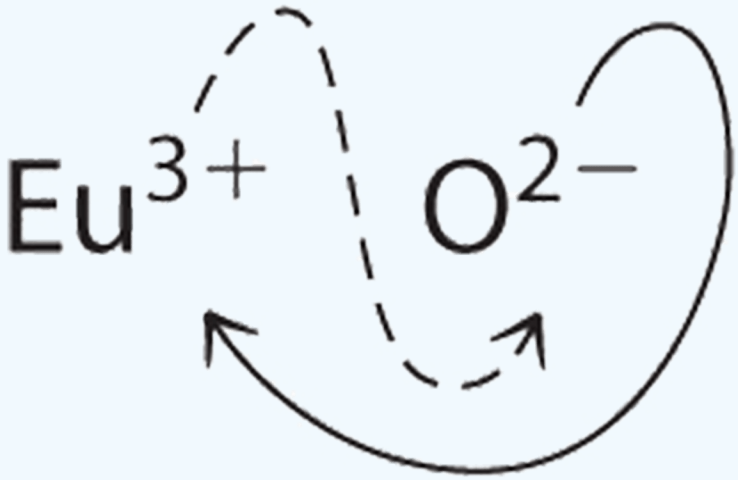
Solution

a. **B** Using the absolute values of the charges on the ions as the subscripts gives Ga_3As_3:



Reducing the subscripts to the smallest whole numbers gives the empirical formula GaAs, which is electrically neutral [+3 + (−3) = 0]. Alternatively, we could recognize that Ga^{3+} and As^{3-} have charges of equal magnitude but opposite signs. One Ga^{3+} ion balances the charge on one As^{3-} ion, and a 1:1 compound will have no net charge. Because we write subscripts only if the number is greater than 1, the empirical formula is GaAs. GaAs is gallium arsenide, which is widely used in the electronics industry in transistors and other devices.

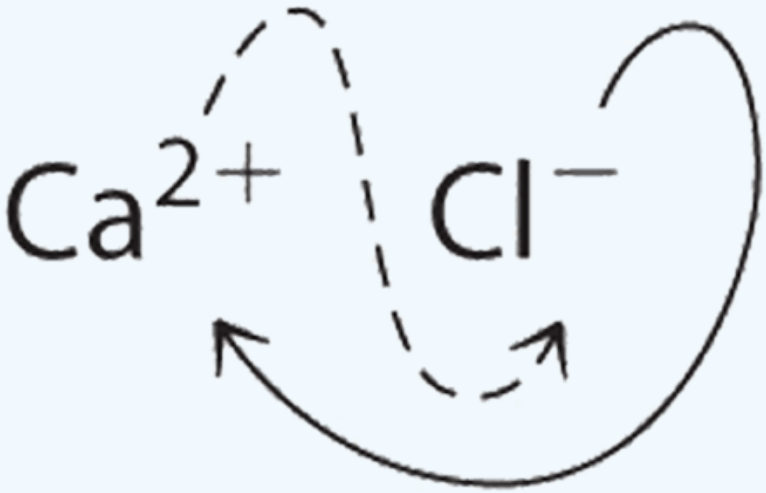
b. **B** Because Eu^{3+} has a charge of +3 and O^{2-} has a charge of −2, a 1:1 compound would have a net charge of +1. We must therefore find multiples of the charges that cancel. We cross charges, using the absolute value of the charge on one ion as the subscript for the other ion:



The subscript for Eu^{3+} is 2 (from O^{2-}), and the subscript for O^{2-} is 3 (from Eu^{3+}), giving Eu_2O_3; the subscripts cannot be reduced further. The empirical formula contains a positive charge of 2(+3) = +6 and a negative charge of 3(−2) = −6, for a net charge of 0. The compound Eu_2O_3 is neutral. Europium oxide is responsible for the red color in television and computer screens.

c. **A** Because the charges on the ions are not given, we must first determine the charges expected for the most common ions derived from calcium and chlorine. Calcium lies in group 2, so it should lose two electrons to form Ca^{2+}. Chlorine lies in group 17, so it should gain one electron to form Cl^-.

B Two Cl^- ions are needed to balance the charge on one Ca^{2+} ion, which leads to the empirical formula $CaCl_2$. We could also cross charges, using the absolute value of the charge on Ca^{2+} as the subscript for Cl and the absolute value of the charge on Cl^- as the subscript for Ca:



The subscripts in $CaCl_2$ cannot be reduced further. The empirical formula is electrically neutral [+2 + 2(−1) = 0]. This compound is calcium chloride, one of the substances used as “salt” to melt ice on roads and sidewalks in winter.

Exercise 2.8.1

Write the empirical formula for the simplest binary ionic compound formed from each ion or element pair.

a. Li^+ and N^{3-}
b. Al^{3+} and O^{2-}
c. lithium and oxygen

Answer a available at the end of this section.

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Polyatomic Ions

Polyatomic ions are groups of atoms that bear net electrical charges, although the atoms in a polyatomic ion are held together by the same covalent bonds that hold atoms together in molecules. Just as there are many more kinds of molecules than simple elements, there are many more kinds of polyatomic ions than monatomic ions. Two examples of polyatomic cations are the ammonium (NH_4^+) and the methylammonium ($CH_3NH_3^+$) ions. Polyatomic anions are much more numerous than polyatomic cations; some common examples are in Table 2.8.1.

Table 2.8.1: Common Polyatomic Ions and Their Names

Formula	Name of Ion	Formula	Name of Ion
NH_4^+	ammonium	HPO_4^{2-}	hydrogen phosphate
$CH_3NH_3^+$	methylammonium	$H_2PO_4^-$	dihydrogen phosphate
OH^-	hydroxide	ClO^-	hypochlorite
O_2^{2-}	peroxide	ClO_2^-	chlorite
CN^-	cyanide	ClO_3^-	chlorate
SCN^-	thiocyanate	ClO_4^-	perchlorate
NO_2^-	nitrite	MnO_4^-	permanganate
NO_3^-	nitrate	$CrO4_2^-$	chromate
CO_3^{2-}	carbonate	$Cr_2O_7^{2-}$	dichromate
HCO_3^-	hydrogen carbonate, or bicarbonate	$C_2O_4^{2-}$	oxalate
SO_3^{2-}	sulfite	HCO_2^-	formate
SO_4^{2-}	sulfate	$CH_3CO_2^-$	acetate
HSO_4^-	hydrogen sulfate, or bisulfate	$C_6H_5CO_2^-$	benzoate
PO_4^{3-}	phosphate		

The method used to predict the empirical formulas for ionic compounds that contain monatomic ions can also be used for compounds that contain polyatomic ions. The overall charge on the cations must balance the overall charge on the anions in the formula unit. Thus, K^+ and NO_3^- ions combine in a 1:1 ratio to form KNO_3 (potassium nitrate or saltpeter), a major ingredient in black gunpowder. Similarly, Ca^{2+} and SO_4^{2-} form $CaSO_4$ (calcium sulfate), which combines with varying amounts of water to form gypsum and plaster of Paris. The polyatomic ions NH_4^+ and NO_3^- form NH_4NO_3 (ammonium nitrate), a widely used fertilizer and, in the wrong hands, an explosive. One example of a compound in which the ions have charges of different magnitudes is calcium phosphate, which is composed of Ca^{2+} and PO_4^{3-} ions; it is a major component of bones. The compound is electrically neutral because the ions combine in a ratio of three Ca^{2+} ions [3(+2) = +6] for every two ions [2(−3) = −6], giving an empirical formula of $Ca_3(PO_4)_2$; the parentheses around PO_4 in the empirical formula indicate that it is a polyatomic ion. Writing the formula for calcium phosphate as $Ca_3P_2O_8$ gives the correct number of each atom in the formula unit, but it obscures the fact that the compound contains readily identifiable PO_4^{3-} ions.

Example 2.8.2

Write the empirical formula for the compound formed from each ion pair.

a. Na^+ and HPO_4^{2-}
b. potassium cation and cyanide anion
c. calcium cation and hypochlorite anion

Given: ions

Asked for: empirical formula for ionic compound

Strategy:

A. If it is not given, determine the charge on a monatomic ion from its location in the periodic table. Use Table 2.8.1 to find the charge on a polyatomic ion.
B. Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the smallest whole numbers when writing the empirical formula.

Solution:

a. **B** Because HPO_4^{2-} has a charge of –2 and Na^+ has a charge of +1, the empirical formula requires two Na^+ ions to balance the charge of the polyatomic ion, giving Na_2HPO_4. The subscripts are reduced to the lowest numbers, so the empirical formula is Na_2HPO_4. This compound is sodium hydrogen phosphate, which is used to provide texture in processed cheese, puddings, and instant breakfasts.
b. **A** The potassium cation is K^+, and the cyanide anion is CN^-. **B** Because the magnitude of the charge on each ion is the same, the empirical formula is KCN. Potassium cyanide is highly toxic, and at one time it was used as rat poison. This use has been discontinued, however, because too many people were being poisoned accidentally.
c. **A** The calcium cation is Ca^{2+}, and the hypochlorite anion is ClO^-. **B** Two ClO^- ions are needed to balance the charge on one Ca^{2+} ion, giving $Ca(ClO)_2$. The subscripts cannot be reduced further, so the empirical formula is $Ca(ClO)_2$. This is calcium hypochlorite, the “chlorine” used to purify water in swimming pools.

Exercise 2.8.2

Write the empirical formula for the compound formed from each ion pair.

a. Ca^{2+} and $H_2PO_4^-$
b. sodium cation and bicarbonate anion
c. ammonium cation and sulfate anion

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Hydrates

Many ionic compounds occur as hydrates, compounds that contain specific ratios of loosely bound water molecules, called waters of hydration. Waters of hydration can often be removed simply by heating. For example, calcium dihydrogen phosphate can form a solid that contains one molecule of water per $Ca(H_2PO_4)_2$ unit and is used as a leavening agent in the food industry to cause baked goods to rise. The empirical formula for the solid is $Ca(H_2PO_4)_2 \cdot H_2O$. In contrast, copper sulfate usually forms a blue solid that contains five waters of hydration per formula unit, with the empirical formula $CuSO_4 \cdot 5\,H_2O$. When heated, all five water molecules are lost, giving a white solid with the empirical formula $CuSO_4$.



Figure 2.8.1: Loss of Water from a Hydrate with Heating. (left) When blue $CuSO_4 \cdot 5H_2O$ is heated, two molecules of water are lost at 30°C, two more at 110°C, and the last at 250°C to give white "anhydrous" $CuSO_4$ (right). Images used with permission from Wikipedia.

Compounds that differ only in the numbers of waters of hydration can have very different properties. For example, $\mathrm{CaSO_4 \cdot ½H_2O}$ is *plaster of Paris*, which was often used to make sturdy casts for broken arms or legs, whereas $\mathrm{CaSO_4 \cdot 2\,H_2O}$ is the less dense, flakier gypsum, a mineral used in drywall panels for home construction. When a cast would set, a mixture of plaster of Paris and water crystallized to give solid $\mathrm{CaSO_4 \cdot 2\,H_2O}$. Similar processes are used in the setting of cement and concrete.

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a binary acid (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word "acid" is added as a second word

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table 2.8.2.

Table 2.8.2: Names of Some Simple Acids

Name of Gas	Name of Acid
HF(*g*), hydrogen fluoride	HF(*aq*), hydrofluoric acid
HCl(*g*), hydrogen chloride	HCl(*aq*), hydrochloric acid
HBr(*g*), hydrogen bromide	HBr(*aq*), hydrobromic acid
HI(*g*), hydrogen iodide	HI(*aq*), hydroiodic acid
H_2S(*g*), hydrogen sulfide	H_2S(*aq*), hydrosulfuric acid

Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as oxyacids, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit “hydrogen”
2. Start with the root name of the anion
3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add “acid”

For example, consider H_2CO_3 (which you might be tempted to call “hydrogen carbonate”). To name this correctly, “hydrogen” is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table 2.8.3. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table 2.8.3: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

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Bases

We will present more comprehensive definitions of bases in later chapters, but virtually every base you encounter in the meantime will be an ionic compound, such as sodium hydroxide (NaOH) and barium hydroxide [$Ba(OH)_2$], that contain the hydroxide ion and a metal cation. These have the general formula $M(OH)_n$. It is important to recognize that alcohols, with the general formula ROH, are covalent compounds, not ionic compounds; consequently, they do *not* dissociate in water to form a basic solution (containing OH^- ions). When a base reacts with any of the acids we have discussed, it accepts a proton (H^+). For example, the hydroxide ion (OH^-) accepts a proton to form H_2O. Thus bases are also referred to as *proton acceptors*.

Concentrated aqueous solutions of ammonia (NH_3) contain significant amounts of the hydroxide ion, even though the dissolved substance is *not* primarily ammonium hydroxide (NH_4OH) as is often stated on the label. Thus aqueous ammonia solution is also a common base. Replacing a hydrogen atom of NH_3 with an alkyl group results in an amine (RNH_2), which is also a base. Amines have pungent odors—for example, methylamine (CH_3NH_2) is one of the compounds responsible for the foul odor associated with spoiled fish. The physiological importance of amines is suggested in the word *vitamin*, which is derived from the phrase *vital amines*. The word was coined to describe dietary substances that were effective at preventing scurvy, rickets, and other diseases because these substances were assumed to be amines. Subsequently, some vitamins have indeed been confirmed to be amines.

Binary Inorganic Compounds

Binary covalent compounds—covalent compounds that contain only two elements—are named using a procedure similar to that used for simple ionic compounds, but prefixes are added as needed to indicate the number of atoms of each kind. The procedure, diagrammed in Figure $2.8.2$ consists of the following steps:

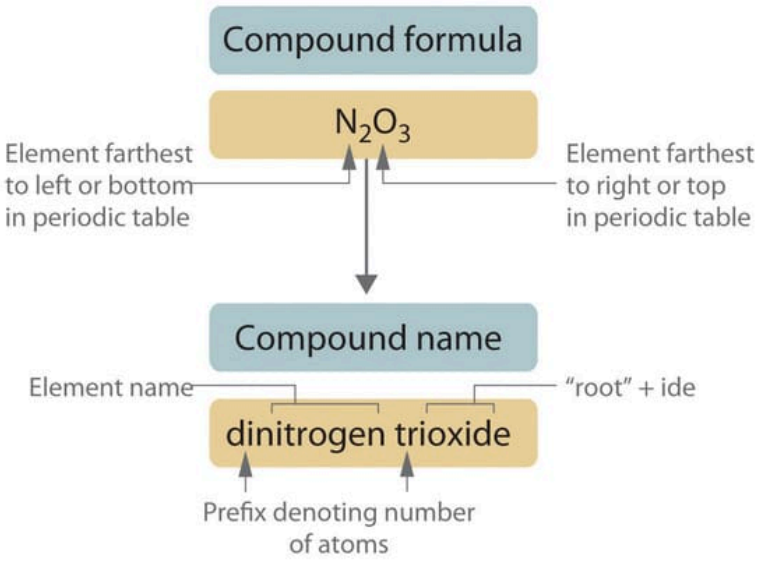


Figure 2.8.2: Naming a Covalent Inorganic Compound

Breakdown of formula names and compound formula. The atom farthest to the left on the periodic table is named first.

1. Place the elements in their proper order.
   - The element farthest to the left in the periodic table is usually named first. If both elements are in the same group, the element closer to the bottom of the column is named first.
   - The second element is named as if it were a monatomic anion in an ionic compound (even though it is not), with the suffix *-ide* attached to the root of the element name.
2. Identify the number of each type of atom present.
   1. Prefixes derived from Greek stems are used to indicate the number of each type of atom in the formula unit (Table 2.8.3). The prefix *mono-* ("one") is used only when absolutely necessary to avoid confusion, just as the subscript 1 is omitted when writing molecular formulas.

      To demonstrate steps 1 and 2a, HCl is named hydrogen chloride (because hydrogen is to the left of chlorine in the periodic table), and PCl_5 is phosphorus pentachloride. The order of the elements in the name of BrF_3, bromine trifluoride, is determined by the fact that bromine lies below fluorine in Group 17.

Table 2.8.3: Prefixes for Indicating the Number of Atoms in Chemical Names

Prefix	Number
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10
undeca-	11
dodeca-	12

2. If a molecule contains more than one atom of both elements, then prefixes are used for both. Thus N_2O_3 is *di*nitrogen *tri*oxide, as shown in Figure 2.13.
3. In some names, the final *a* or *o* of the prefix is dropped to avoid awkward pronunciation. Thus OsO_4 is osmium tetroxide rather than osmium tetraoxide.

3. Write the name of the compound.
   1. Binary compounds of the elements with oxygen are generally named as "element oxide," with prefixes that indicate the number of atoms of each element per formula unit. For example, CO is carbon monoxide. The only exception is binary compounds of oxygen with fluorine, which are named as oxygen fluorides.
   2. Certain compounds are *always* called by the common names that were assigned before formulas were used. For example, H_2O is water (not dihydrogen oxide); NH_3 is ammonia; PH_3 is phosphine; SiH_4 is silane; and B_2H_6, a *dimer* of BH_3, is diborane. For many compounds, the systematic name and the common name are both used frequently, requiring familiarity with both. For example, the systematic name for NO is nitrogen monoxide, but it is much more commonly called nitric oxide. Similarly, N_2O is usually called nitrous oxide rather than dinitrogen monoxide. Notice that the suffixes *-ic* and *-ous* are the same ones used for ionic compounds.

Start with the element at the far left in the periodic table and work to the right. If two or more elements are in the same group, start with the bottom element and work up.

Example 2.8.3: Binary Covalent Compounds

Write the name of each binary covalent compound.

a. SF_6
b. N_2O_4
c. ClO_2

Given: molecular formula

Asked for: name of compound

Strategy:

A. List the elements in order according to their positions in the periodic table. Identify the number of each type of atom in the chemical formula and then use Table 2.8.2 to determine the prefixes needed.
B. If the compound contains oxygen, follow step 3a. If not, decide whether to use the common name or the systematic name.

Solution:

a. **A** Because sulfur is to the left of fluorine in the periodic table, sulfur is named first. Because there is only one sulfur atom in the formula, no prefix is needed. **B** There are, however, six fluorine atoms, so we use the prefix for six: *hexa-* (Table 2.8.2). The compound is sulfur hexafluoride.
b. **A** Because nitrogen is to the left of oxygen in the periodic table, nitrogen is named first. Because more than one atom of each element is present, prefixes are needed to indicate the number of atoms of each. According to Table 2.8.2 "Prefixes for Indicating the Number of Atoms in Chemical Names", the prefix for two is *di-*, and the prefix for four is *tetra-*. **B** The compound is dinitrogen tetroxide (omitting the *a* in *tetra-* according to step 2c) and is used as a component of some rocket fuels.

c. **A** Although oxygen lies to the left of chlorine in the periodic table, it is not named first because ClO_2 is an oxide of an element other than fluorine (step 3a). Consequently, chlorine is named first, but a prefix is not necessary because each molecule has only one atom of chlorine. **B** Because there are two oxygen atoms, the compound is a dioxide. Thus the compound is chlorine dioxide. It is widely used as a substitute for chlorine in municipal water treatment plants because, unlike chlorine, it does not react with organic compounds in water to produce potentially toxic chlorinated compounds.

Example 2.8.3

Write the name of each binary covalent compound.

a. IF_7
b. N_2O_5
c. OF_2

Answer a available at the end of this section.

Example 2.8.4

Write the formula for each binary covalent compound.

a. sulfur trioxide
b. diiodine pentoxide

Given: name of compound

Asked for: formula

Strategy:

List the elements in the same order as in the formula, use Table 2.8.2 to identify the number of each type of atom present, and then indicate this quantity as a subscript to the right of that element when writing the formula.

Solution:

a. Sulfur has no prefix, which means that each molecule has only one sulfur atom. The prefix *tri-* indicates that there are three oxygen atoms. The formula is therefore SO_3. Sulfur trioxide is produced industrially in huge amounts as an intermediate in the synthesis of sulfuric acid.
b. The prefix *di-* tells you that each molecule has two iodine atoms, and the prefix *penta-* indicates that there are five oxygen atoms. The formula is thus I_2O_5, a compound used to remove carbon monoxide from air in respirators.

Exercise 2.8.4

Write the formula for each binary covalent compound.

a. silicon tetrachloride
b. disulfur decafluoride

Answer a available at the end of this section.

The structures of some of the compounds in Examples 2.8.3 and 2.8.4 are shown in Figure 2.8.2 along with the location of the "central atom" of each compound in the periodic table. It may seem that the compositions and structures of such compounds are entirely random, but this is not true. After mastering the material discussed later on this course, one is able to predict the compositions and structures of compounds of this type with a high degree of accuracy.

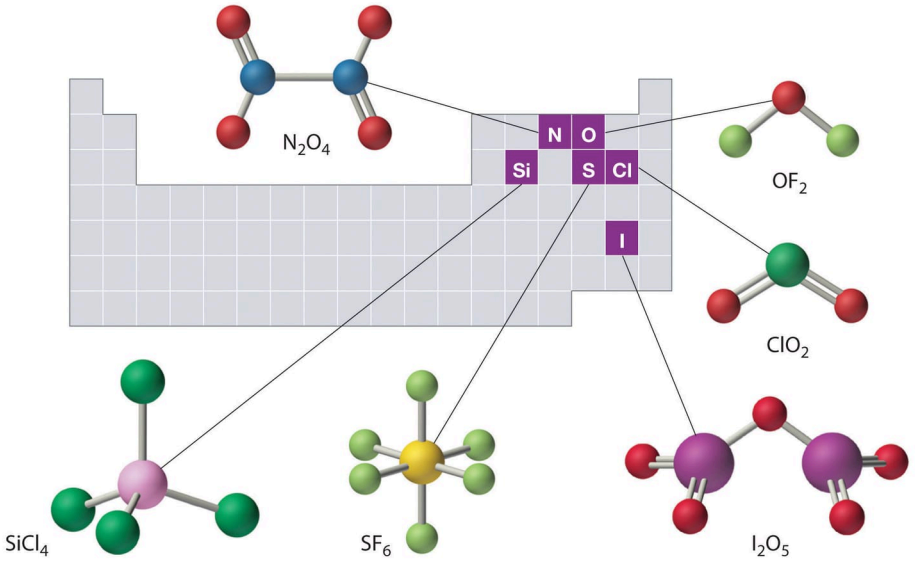


Figure 2.8.2: The Structures of Some Covalent Inorganic Compounds and the Locations of the “Central Atoms” in the Periodic Table. The compositions and structures of covalent inorganic compounds are not random and can be predicted from the locations of the component atoms in the periodic table.

Central atoms of compounds N 2 O 4, O F 2, C l O 2, I 2 O 5, S F 6, and S i C l 4 shown on the periodic table.

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Nomenclature of Nonmetals: Nomenclature of Nonmetals, YouTube(opens in new window) [youtu.be] (opens in new window)

Summary

The composition of a compound is represented by an empirical or molecular formula, each consisting of at least one formula unit. Covalent inorganic compounds are named using a procedure similar to that used for ionic compounds, whereas hydrocarbons use a system based on the number of bonds between carbon atoms. Covalent inorganic compounds are named by a procedure similar to that used for ionic compounds, using prefixes to indicate the numbers of atoms in the molecular formula. An empirical formula gives the relative numbers of atoms of the elements in a compound, reduced to the lowest whole numbers. The formula unit is the absolute grouping represented by the empirical formula of a compound, either ionic or covalent. Empirical formulas are particularly useful for describing the composition of ionic compounds, which do not contain readily identifiable molecules. Some ionic compounds occur as hydrates, which contain specific ratios of loosely bound water molecules called waters of hydration.

Answers

Exercise 2.8.1

Li_3N

Al_2O_3

Li_2O

Exercise 2.8.2

$Ca(H_2PO_4)_2$: calcium dihydrogen phosphate is one of the ingredients in baking powder.

$NaHCO_3$: sodium bicarbonate is found in antacids and baking powder; in pure form, it is sold as baking soda.

$(NH_4)_2SO_4$: ammonium sulfate is a common source of nitrogen in fertilizers.

Example 2.8.3

iodine heptafluoride

dinitrogen pentoxide

oxygen difluoride

Exercise 2.8.4

$SiCl_4$

S_2F_{10}

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2.9: Some Simple Organic Compounds

Learning Objectives

- To be familiar with the classes of basic organic chemistry compounds

Approximately one-third of the compounds produced industrially are organic compounds. All living organisms are composed of organic compounds, as are most foods, medicines, clothing fibers, and plastics. The detection of organic compounds is useful in many fields. In one recently developed application, scientists have devised a new method called “material degradomics” to monitor the degradation of old books and historical documents. As paper ages, it produces a familiar “old book smell” from the release of organic compounds in gaseous form. The composition of the gas depends on the original type of paper used, a book’s binding, and the applied media. By analyzing these organic gases and isolating the individual components, preservationists are better able to determine the condition of an object and those books and documents most in need of immediate protection.

The simplest class of organic compounds is the hydrocarbons, which consist entirely of carbon and hydrogen. Petroleum and natural gas are complex, naturally occurring mixtures of many different hydrocarbons that furnish raw materials for the chemical industry. The four major classes of hydrocarbons are the following: the alkanes, which contain only carbon–hydrogen and carbon–carbon single bonds; the alkenes, which contain at least one carbon–carbon double bond; the alkynes, which contain at least one carbon–carbon triple bond; and the aromatic hydrocarbons, which usually contain rings of six carbon atoms that can be drawn with alternating single and double bonds. Alkanes are also called saturated hydrocarbons, whereas hydrocarbons that contain multiple bonds (alkenes, alkynes, and aromatics) are unsaturated.

Alkanes

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2.E: Atoms, Molecules, and Ions (Exercises)

2.1: The Atomic Theory of Matter

Conceptual Problems

1. Which of the following elements exist as diatomic molecules?

    a. helium
    b. hydrogen
    c. iodine
    d. gold

2. Which of the following elements exist as diatomic molecules?

    a. chlorine
    b. potassium
    c. silver
    d. oxygen

3. Why is it proper to represent the elemental form of helium as He but improper to represent the elemental form of hydrogen as H?

4. Why is it proper to represent the elemental form of chlorine as Cl_2 but improper to represent the elemental form of calcium as Ca_2?

Conceptual Solutions

1. Hydrogen and Iodine.
2. Chlorine and Oxygen.
3. Hydrogen exists as a diatomic molecule in its elemental form; helium does not exist as a diatomic molecule.
4. Chlorine exists naturally in its diatomic form, while Calcium does not.

2.2: The Discovery of Atomic Structure

Exercises

1. What is the modern atomic theory?
2. What are atoms?

Conceptual Answers

1. The modern atomic theory states that all matter is composed of atoms, which are unique between elements. They cannot be created or destroyed, but can combine with one another in whole number ratios to form compounds.
2. Atoms are the smallest parts of an element that maintain the identity of that element.

Numerical Problems

1. (Basic concept check) When 32.0 grams (g) of methane are burned in 128.0 g of oxygen, 88.0 g of carbon dioxide and 72.0 g of water are produced. Which law is this an example of? (a) Law of definite proportions (b) Law of conservation of mass or

(c) Law of multiple proportions.

2. (Law of Conservation of Mass) 8.00 grams (g) of methane are burned in 32.00 g of oxygen. The reaction produces 22.00 g of carbon dioxide and an unmeasured mass of water. What mass of water is produced?
3. (Law of Definite Proportions) Two experiments using sodium and chlorine are performed. In the first experiment, 4.36 grams (g) sodium are reacted with 32.24 g of chlorine, using up all the sodium. 11.08 g of sodium chloride was produced in the first experiment. In the second experiment, 4.20 g of chlorine reacted with 20.00 g of sodium, using up all the chlorine. 6.92 g of sodium chloride was produced in the second experiment. Show that these results are consistent with the law of constant composition.
4. (Law of Conservation of Mass): 36.0 grams (g) of wood are burned in oxygen. The products of this reaction weigh 74.4 g. (a) What mass of oxygen is needed in this reaction? (b) What mass of oxygen is needed to burn 8.00 lb of wood? 1 lb = 453.59237 g.
5. (Law of Definite Proportions): A sample of methane contains only carbon and hydrogen, with 3.00 grams (g) of carbon for every 1.00 g of hydrogen. How much hydrogen should be present in a different, 50.0 g same of methane?

Numerical Solutions

1. The answer is (b) Law of conservation of mass. The number of grams of reactants (32.0 g of methane and 128.0 g of oxygen = 160.0 g total) is equal to the number of grams of product (88.0 g of carbon dioxide and 72.0 g of water = 160.0 g total).
2. The answer is 18.00 g of water. Because the only products are water and carbon dioxide, their total mass must equal the total mass of the reactants, methane and oxygen. 8.00 g of methane + 32.00 g of oxygen = 40.00 total g of reactants. Because the total mass of the reactants equals the total mass of the products, the total mass of the products is also 40.00 g. Thus, 40.00 total g of products = 22.00 g carbon dioxide + unknown mass water. 40.00 total g of products - 22.00 g carbon dioxide = 18.00 g water.

3. To solve, determine the percent of sodium in each sample of sodium chloride. There is 4.36 g sodium for every 11.08 g of sodium chloride in the first experiment. The amount of sodium in the sodium chloride for the second experiment must be found. This is found by subtracted the known amount of reacted chlorine (4.20 g) from the amount of sodium chloride (6.92 g). 6.92 g sodium chloride - 4.20 g chlorine = 2.72 g sodium.

   Thus, the percent of sodium in each sample is represented below:
   % Na = (4.36 g Na)/(11.08 g NaCl) x 100% = 39.4% Na % Na = (2.72 g Na)/(6.92 g NaCl) x 100% = 39.3%
   The slight difference in compositions is due to significant figures: each percent has an uncertainty of .01% in either direction. The two samples of sodium chloride have the same composition.

4. a. The answer is 38.4 g of oxygen. The total mass of the products is 74.4 g. Thus, the total mass of the reactants must equal 74.4 g as well. Thus, 74.4 g products - 36.0 g wood reactant = 38.4 g oxygen reactant.
   b. The answer is 8.53 lb of oxygen. From, (a) that it takes 38.4 g of oxygen to burn 18.0 g of wood. First, convert both of these values to pounds (alternatively, the 8.00 lb can be converted to grams).

   36.0 g wood x (1lb)/(453.59237 g) = 0.0793664144 lb wood
   38.4 g oxygen x (1 lb)/(453.59237 g) = .0846575087 lb oxygen

   Now two ratios equal to each other can be set up to determine the unknown mass of oxygen.

   (0.0793664144 lb wood)/(.0846575087 lb oxygen) = (8.00 lb wood)/(unknown mass oxygen)
   Solving reveals that it requires 8.53 lb of oxygen to burn 8.00 lb of wood.

5. The answer is 12.5 g of hydrogen. If there are 3.00 g of carbon present for every 1.00 g of hydrogen, we can assume the smallest whole number combination of these elements in that ratio to be 4.00 g of methane:
   50.0 g methane x (1.00 g hydrogen)/(4.00 g methane) = 12.5 g of hydrogen.

2.3: The Modern View of Atomic Structure

Conceptual Problems

1. Describe the experiment that provided evidence that the proton is positively charged.
2. What observation led Rutherford to propose the existence of the neutron?

3. What is the difference between Rutherford's model of the atom and the model chemists use today?
4. If cathode rays are not deflected when they pass through a region of space, what does this imply about the presence or absence of a magnetic field perpendicular to the path of the rays in that region?
5. Describe the outcome that would be expected from Rutherford's experiment if the charge on α particles had remained the same but the nucleus were negatively charged. If the nucleus were neutral, what would have been the outcome?
6. Describe the differences between an α particle, a β particle, and a γ ray. Which has the greatest ability to penetrate matter?

Conceptual Solutions

1. Ernest Rutherford's 1911 Alpha-ray scattering experiment proved that the nucleus of an atom is positively charged. In the experiment, he fired high-energy streams of α particles at a thin gold sheet. Many passed through unimpeded, but some were deflected slightly and few were reflected back, proving that the positive charge of an atom is contained in the nucleus.
2. Rutherford proposed the existence of the neutron when discovering that electrons and protons alone did not fully account for the mass of the atom, leading him to work with James Chadwick to prove the existence of a neutral particle.
3. While Rutherford's model established the positively charged nucleus surrounded by negatively charged electrons, it stated that the electrons were evenly distributed throughout, rather than in "specific energy levels" of electrons, which are a significant part of the modern model.
4. In the absence of any other fields affecting the cathode ray, a lack of deflection implies an absence of a magnetic field in a direction that would affect their path.
5. If the nucleus were negatively charged, one could expect α particles to be deflected *towards* the nucleus rather than away. If it were neutral, it would have no effect on the particles.
6. α particles are helium nuclei (effectively He ions lacking electrons), β particle are fast-moving electrons, and γ rays are very short electromagnetic rays. Out of the three, γ rays have the greatest penetrative ability.

Numerical Problems

Please be sure you are familiar with the topics discussed in Section 1.6 before proceeding to the Numerical Problems.

1. Using the data in Table 1.3 and the periodic table, calculate the percentage of the mass of a silicon atom that is due to
   a. electrons.
   b. protons.

2. Using the data in Table 1.3 and the periodic table, calculate the percentage of the mass of a helium atom that is due to
   a. electrons.
   b. protons.

3. The radius of an atom is approximately 10^4 times larger than the radius of its nucleus. If the radius of the nucleus were 1.0 cm, what would be the radius of the atom in centimeters? in miles?
4. The total charge on an oil drop was found to be 3.84×10^{-18} coulombs. What is the total number of electrons contained in the drop?

Numerical Solutions

1. The total atomic mass of a silicon atom is 28.085amu. Using the data from the table (as well as silicon's atomic number of 14), we can calculate that the mass of electrons in the atom is 0.0076804amu, while the mass of protons is 14.101864amu. From this we can calculate that electrons take up 0.02735% of the mass of the atom, while protons take up 50.2114% of the atom's mass.
2. The total atomic mass of a helium atom is 4.0026amu. Using the data from the table we see that the mass of electrons in the atom is 0.0010972amu, while the mass of protons is 2.015amu. Therefore, electrons take up 0.0274% of the mass of the atom, while protons take up 50.342%.
3. If the nucleus were to have a radius of 1.0cm, the atom would have a radius of 10000cm, or 0.06 miles.
4. The electrical charge of a single electron is equal to -1.602×10^{-19}. Thus, we can divide the total charge of the oil drop by this number to see that there are 24 electrons contained within it.

2.4: Atomic Mass

Conceptual Problems

1. Complete the following table for the missing elements, symbols, and numbers of electrons.

Element	Symbol	Number of Electrons
molybdenum		
		19
titanium		
	B	
		53
	Sm	
helium		
		14

2. Complete the following table for the missing elements, symbols, and numbers of electrons.

Element	Symbol	Number of Electrons
lanthanum		
	Ir	
aluminum		
		80
sodium		
	Si	
		9
	Be	

3. Is the mass of an ion the same as the mass of its parent atom? Explain your answer.

4. What isotopic standard is used for determining the mass of an atom?

5. Give the symbol ${}^{A}_{Z}X$ for these elements, all of which exist as a single isotope.

a. beryllium
b. ruthenium
c. phosphorus
d. aluminum
e. cesium
f. praseodymium
g. cobalt
h. yttrium
i. arsenic

6. Give the symbol ${}^{A}_{Z}X$ for these elements, all of which exist as a single isotope.

a. fluorine
b. helium
c. terbium
d. iodine
e. gold

f. scandium
g. sodium
h. niobium
i. manganese

7. Identify each element, represented by X, that has the given symbols.

a. $^{55}_{26}X$
b. $^{74}_{33}X$
c. $^{24}_{12}X$
d. $^{127}_{53}X$
e. $^{40}_{18}X$
f. $^{152}_{63}X$

Conceptual Solutions

1.

Element	Symbol	Number of Electrons
molybdenum	Mo	42
potassium	K	19
titanium	Ti	22
boron	B	5
iodine	I	53
samarium	Sm	62
helium	He	2
silicon	Si	14

2.

Element	Symbol	Number of Electrons
lanthanum	La	57
iridium	Ir	77
aluminum	Al	13
mercury	Hg	80
sodium	Na	11
silicon	Si	14
flourine	F	9
beryllium	Be	4

3. Although the mass of an ion is not *exactly* the same as its parent atom, electrons weigh so little that removing them will not change the mass in any significant way. Thus, we can say that the mass of an ion is the same.
4. The reference isotope which is used for determining the mass of all other atoms is the carbon-12 nuclide, which is set to weigh exactly 12 amu. Therefore other elements are massed in relation to this value.
5. Give the symbol $^{A}_{Z}X$ for these elements, all of which exist as a single isotope.
    1. beryllium
        1. $^{9}_{4}Be$
    2. ruthenium
        1. $^{102}_{44}Ru$
    3. phosphorus
        1. $^{31}_{15}P$
    4. aluminum

    1. $^{27}_{13}Al$
5. cesium
    1. $^{133}_{55}Cs$
6. praseodymium
    1. $^{141}_{59}Pr$
7. cobalt
    1. $^{59}_{27}Co$
8. yttrium
    1. $^{89}_{39}Y$
9. arsenic
    1. $^{75}_{33}As$

6. Give the symbol $^{A}_{Z}X$ for these elements.

    1. fluorine

        1. $^{19}_{9}F$

    2. helium

        1. $^{4}_{2}He$

    3. terbium
        1. $^{159}_{65}Tb$
    4. iodine
        1. $^{127}_{53}I$
    5. gold
        1. $^{197}_{79}Au$
    6. scandium
        1. $^{45}_{21}Sc$
    7. sodium
        1. $^{23}_{11}Na$
    8. niobium
        1. $^{93}_{41}Nb$
    9. manganese
        1. $^{55}_{25}Mn$

7. Identify each element, represented by X, that has the given symbols.

    1. $^{55}_{26}X$
        1. Iron (Fe)
    2. $^{74}_{33}X$
        1. Arsenic (As)
    3. $^{24}_{12}X$
        1. Magnesium (Mg)
    4. $^{127}_{53}X$
        1. Iodine (I)
    5. $^{40}_{18}X$
        1. Argon (Ar)
    6. $^{152}_{63}X$
        1. Europium (Eu)

Numerical Problems

Please be sure you are familiar with the topics discussed in Section 1.6 before proceeding to the Numerical Problems.

1. The isotopes ^{131}I and ^{60}Co are commonly used in medicine. Determine the number of neutrons, protons, and electrons in a neutral atom of each.

2. Determine the number of protons, neutrons, and electrons in a neutral atom of each isotope:

a. ^{97}Tc
b. ^{113}In
c. ^{63}Ni
d. ^{55}Fe

3. Both technetium-97 and americium-240 are produced in nuclear reactors. Determine the number of protons, neutrons, and electrons in the neutral atoms of each.

4. The following isotopes are important in archeological research. How many protons, neutrons, and electrons does a neutral atom of each contain?

a. ^{207}Pb
b. ^{16}O
c. ^{40}K
d. ^{137}Cs
e. ^{40}Ar

5. Copper, an excellent conductor of heat, has two isotopes: ^{63}Cu and ^{65}Cu. Use the following information to calculate the average atomic mass of copper:

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{63}Cu	69.09	62.9298
^{65}Cu	30.92	64.9278

6. Silicon consists of three isotopes with the following percent abundance:

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{28}Si	92.18	27.976926
^{29}Si	4.71	28.976495
^{30}Si	3.12	29.973770

Calculate the average atomic mass of silicon.

7. Complete the following table for neon. The average atomic mass of neon is 20.1797 amu.

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{20}Ne	90.92	19.99244
^{21}Ne	0.257	20.99395
^{22}Ne		

8. Are $^{63}_{28}X$ and $^{62}_{29}X$ isotopes of the same element? Explain your answer.

9.Complete the following table:

Isotope	Number of Protons	Number of Neutrons	Number of Electrons
^{238}X			95
^{238}U			

	75	112	

10.Complete the following table:

Isotope	Number of Protons	Number of Neutrons	Number of Electrons
^{57}Fe			
^{40}X		20	
^{36}S			

11. Using a mass spectrometer, a scientist determined the percent abundances of the isotopes of sulfur to be 95.27% for ^{32}S, 0.51% for ^{33}S, and 4.22% for ^{34}S. Use the atomic mass of sulfur from the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements") and the following atomic masses to determine whether these data are accurate, assuming that these are the only isotopes of sulfur: 31.972071 amu for ^{32}S, 32.971459 amu for ^{33}S, and 33.967867 amu for ^{34}S.

12. The percent abundances of two of the three isotopes of oxygen are 99.76% for ^{16}O, and 0.204% for ^{18}O. Use the atomic mass of oxygen given in the periodic table and the following data to determine the mass of ^{17}O: 15.994915 amu for ^{16}O and 17.999160 amu for ^{18}O.

13. Which element has the higher proportion by mass in NaI?

14. Which element has the higher proportion by mass in KBr?

Numerical Solutions

1. Determine the number of neutrons, protons, and electrons in a neutral atom of:
    1. ^{131}I
        1. 53 Protons, 53 Electrons, 78 Neutrons. In a neutral atom, the amount of protons is equal to the amount of electrons. Additionally, the amount of neutrons can be found by taking [Mass Number] - [Amount of Protons].
    2. ^{60}Co
        1. 27 Protons, 27 Electrons, 33 Neutrons.

2. Determine the number of protons, neutrons, and electrons in a neutral atom of each isotope:

    1. ^{97}Tc
        1. 43 Protons, 43 Electrons, 54 Neutrons
    2. ^{113}In
        1. 49 Protons, 49 Electrons, 64 Neutrons
    3. ^{63}Ni
        1. 28 Protons, 28 Electrons, 35 Neutrons
    4. ^{55}Fe
        1. 26 Protons, 26 Electrons, 29 Neutrons
3. Determine the number of protons, neutrons, and electrons in the neutral atoms of each.
    1. Technetium-97
        1. 43 Protons, 43 Electrons, 54 Neutrons
    2. Americium-240
        1. 95 Protons, 95 Electrons, 145 Neutrons

4. How many protons, neutrons, and electrons does a neutral atom of each contain?

    1. ^{207}Pb
        1. 82 Protons, 82 Electrons, 125 Neutrons
    2. ^{16}O
        1. 8 Protons, 8 Electrons, 8 Neutrons

3. ^{40}K
    1. 19 Protons, 19 Electrons, 21 Neutrons
4. ^{137}Cs
    1. 55 Protons, 55 Electrons, 82 Neutrons
5. ^{40}Ar
    1. 18 Protons, 18 Electrons, 22 Neutrons
5. The average atomic mass of an element from its isotopes can be found via the equation: Average A. Mass = $f_1M_1 + f_2M_2 + ... + f_nM_n$, where f is the abundance of an isotope and M is that isotope's mass. For example, for the given table of copper, we can plug in (0.6909 × 62.9298) + (0.3092 × 64.9278) = 63.5539amu.
6. Average Atomic Mass of Silicon: (0.9218 × 27.796926) + (0.0471 × 28.976495) + (0.0312 × 29.97377) = 27.9232amu.
7.

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{20}Ne	90.92	19.99244
^{21}Ne	0.257	20.99395
^{22}Ne	8.823	22.08568

8. They are not isotopes of the same element, because the number of protons (and therefore the atomic number) are different. For two isotopes to be of the same element, they must share an atomic number.
9.

Isotope	Number of Protons	Number of Neutrons	Number of Electrons
^{238}X	95	143	95
^{238}U	92	146	92
^{187}Re	75	112	75

10.

Isotope	Number of Protons	Number of Neutrons	Number of Electrons
^{57}Fe	26	31	26
^{40}X	20	20	20
^{36}S	16	20	16

11. To solve this problem, we will use the same method we did for problem 6. With the values given we can plug them into the formula to obtain (0.9572 × 31.9720) + (0.0051 × 32.9715) + (0.0422 × 33.9679) = 32.2052amu. The periodic table states that the mass of sulfur is 32.06amu, meaning that the measurements are not entirely accurate.
12. From the given percent abundances, we can calculate that the abundance of ^{17}O is 0.036%. Plugging this into the formula we can solve for the mass of ^{17}O, which is 15.985amu. Obviously, it does not make much sense for an isotope of oxygen containing more neutrons to be lighter, meaning the data is not entirely correct.
13. Iodine has a higher proportion by mass in NaI. For every 22.99amu of Na, there are 126.9amu of I.
14. Bromine has a higher proportion by mass in KBr. For every 39.098amu of K, there are 79.904amu of Br.

2.5: The Periodic Table

Conceptual Problems

1. Classify each element in Conceptual Problem 1 of section 2.4 as a metal, a nonmetal, or a semimetal. If a metal, state whether it is an alkali metal, an alkaline earth metal, or a transition metal.

2. Classify each element in Conceptual Problem 2 of section 2.4 as a metal, a nonmetal, or a semimetal. If a metal, state whether it is an alkali metal, an alkaline earth metal, or a transition metal.

3. Classify each element as a metal, a semimetal, or a nonmetal. If a metal, state whether it is an alkali metal, an alkaline earth metal, or a transition metal.

a. iron
b. tantalum
c. sulfur
d. silicon
e. chlorine
f. nickel
g. potassium
h. radon
i. zirconium

4. Which of these sets of elements are all in the same period?

a. potassium, vanadium, and ruthenium
b. lithium, carbon, and chlorine
c. sodium, magnesium, and sulfur
d. chromium, nickel, and krypton

5. Which of these sets of elements are all in the same period?

a. barium, tungsten, and argon
b. yttrium, zirconium, and selenium
c. potassium, calcium, and zinc
d. scandium, bromine, and manganese

6. Which of these sets of elements are all in the same group?

a. sodium, rubidium, and barium
b. nitrogen, phosphorus, and bismuth
c. copper, silver, and gold
d. magnesium, strontium, and samarium

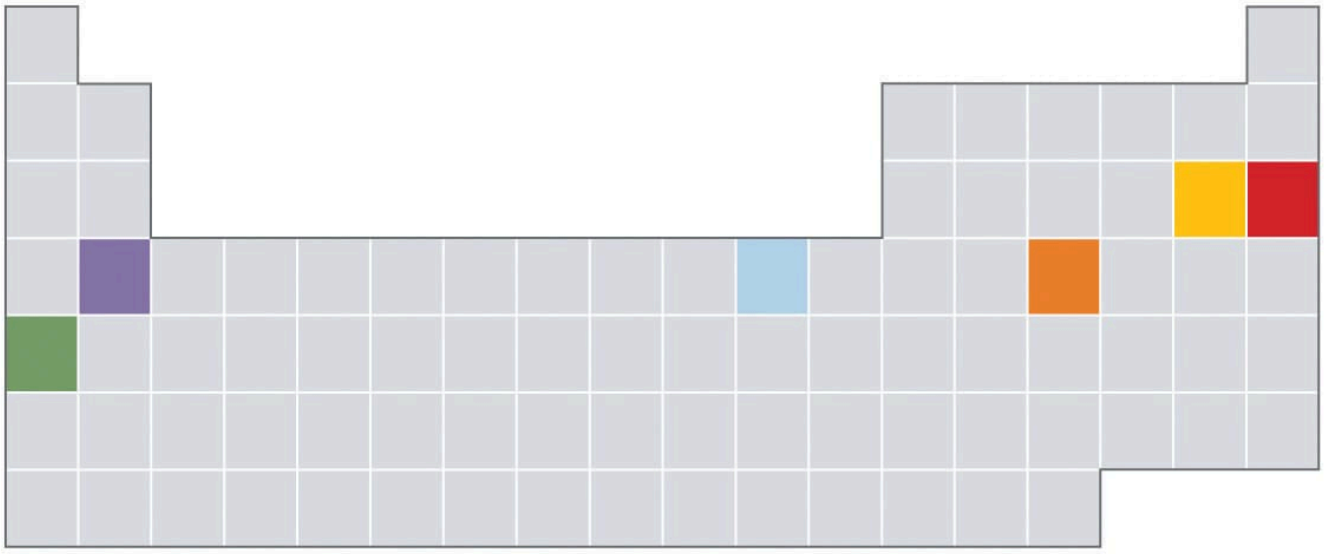
7. Which of these sets of elements are all in the same group?

a. iron, ruthenium, and osmium
b. nickel, palladium, and lead
c. iodine, fluorine, and oxygen
d. boron, aluminum, and gallium

8. Indicate whether each element is a transition metal, a halogen, or a noble gas.

a. manganese
b. iridium
c. fluorine
d. xenon
e. lithium
f. carbon
g. zinc
h. sodium
i. tantalum
j. hafnium
k. antimony
l. cadmium

9. Which of the elements indicated in color in the periodic table shown below is most likely to exist as a monoatomic gas? As a diatomic gas? Which is most likely to be a semimetal? A reactive metal?



10. Based on their locations in the periodic table, would you expect these elements to be malleable? Why or why not?

a. phosphorus
b. chromium
c. rubidium
d. copper
e. aluminum
f. bismuth
g. neodymium

11. Based on their locations in the periodic table, would you expect these elements to be lustrous? Why or why not?

a. sulfur
b. vanadium
c. nickel
d. arsenic
e. strontium
f. cerium
g. sodium

Conceptual Solution

1.

Element	Symbol	Type
molybdenum	Mo	metal; transition metal
potassium	K	metal; alkali metal
titanium	Ti	metal; transition metal
boron	B	semimetal
iodine	I	nonmetal
samarium	Sm	metal; lanthanide
helium	He	nonmetal
silicon	Si	semimetal

2.

Element	Symbol	Type

lanthanum	La	metal; lanthanide
iridium	Ir	metal; transition metal
aluminum	Al	metal; post-transition metal
mercury	Hg	metal; transition metal
sodium	Na	metal; alkali metal
silicon	Si	semimetal
flourine	F	nonmetal
beryllium	Be	metal; alkaline earth metal

3.

Symbol	Type
Fe	metal: transition metal
Ta	metal: transition metal
S	nonmetal
Si	semimetal
Cl	nonmetal (halogen)
Ni	metal: transition metal
K	metal: alkali metal
Rn	nonmetal (noble gas)
Zr	metal: transition metal

4. C and D. All elements in set C are in the 3rd period, and all elements in set D are in the 4th period.
5. C and D. All elements in both of these sets are in the 4th period.
6. B and C. All elements in set B are in group 15, while all elements in set C are in group 11.
7. A and D. All elements in set A are in group 8, and all elements in set D are in group 13.

8.

Element	Symbol	Type
manganese	Mn	transition metal
iridium	Ir	transition metal
flourine	F	halogen
xenon	Xe	noble gas
lithium	Li	alkali metal
carbon	C	nonmetal
zinc	Zn	transition metal
sodium	Na	alkali metal
tantalum	Ta	transition metal
hafnium	Hf	transition metal
antimony	Sb	semimetal
cadmium	Cd	transition metal

9. The red element is most likely to exist as a monoatomic gas, as it is a noble gas meaning that all electrons are paired, and it has no need to bond with itself. The yellow element is most likely to exist as a diatomic gas, as it is in the halogen group meaning it has one unpaired electron. The orange element is most likely to be a semimetal, being within both the group and

period ranges that include semimetals. The green element is most likely to be a reactive metal, as it is in the first group making it an alkali metal.

10. Note that though some elements are *expected* to be malleable based on their position, that is not always the case. For example, Bismuth would be expected to be malleable due to its status as a post-transition metal, but it is in fact brittle.

1.

Element	Expected to be Malleable?	Why?
phosphorus	No	Reactive Nonmetal
chromium	Yes	Transition Metal
rubidium	Yes	Alkali Metal
copper	Yes	Transition Metal
aluminium	Yes	Post-Transition Metal
bismuth	Yes	Post-Transition Metal
neodymium	Yes	Lanthanoid (Metal)

11.

Element	Lustrous?	Why?
sulfur	No	Reactive Nonmetal
vanadium	Yes	Transition Metal
nickel	Yes	Transition Metal
arsenic	Yes	Metalloid
strontium	Yes	Alkaline Earth Metal
cerium	Yes	Lanthanoid (Metal)
sodium	Yes	Alkali Metal

2.6: Molecules and Molecular Compounds

Conceptual Problems

1. Ionic and covalent compounds are held together by electrostatic attractions between oppositely charged particles. Describe the differences in the nature of the attractions in ionic and covalent compounds. Which class of compounds contains pairs of electrons shared between bonded atoms?
2. Which contains fewer electrons than the neutral atom—the corresponding cation or the anion?
3. What is the difference between an organic compound and an inorganic compound?
4. What is the advantage of writing a structural formula as a condensed formula?
5. The majority of elements that exist as diatomic molecules are found in one group of the periodic table. Identify the group.
6. Discuss the differences between covalent and ionic compounds with regard to
   a. a. the forces that hold the atoms together.
   b. b. melting points.
   c. c. physical states at room temperature and pressure.
7. Why do covalent compounds generally tend to have lower melting points than ionic compounds?

Conceptual Answer

1. Ionic compounds are held together by powerful electromagnetic forces, usually caused by a more electronegative atom "taking" an electron from another to become an ion. Covalent compounds, however, share electrons between them in a steady balance between attractive and repulsive charges.
2. Cations, being positively charged, possess fewer electrons than their neutral atoms.
3. Organic compounds involve Carbon and Hydrogen in nearly all cases, while inorganic compounds consist of the other

elements.
4. Condensed formulas can be written out more quickly and easily, and are helpful when showing that multiple atoms are connected to a single one in a compound.
5. Group 17, Halogens
6.

	Covalent	Ionic
Forces	Electrostatic Attraction between Nuclei and Electrons	Electrostatic Attraction between Cations and Anions
Melting Points	Very Low	Very High
Physical States at STP	Liquid/Gas	Solid

7. Covalent compounds generally melt at lower temperatures than ionic compounds because the intermolecular interactions that hold the molecules together in a molecular solid are weaker than the electrostatic attractions that hold oppositely charged ions together in an ionic solid.

Numerical Problems

1. The structural formula for chloroform ($CHCl_3$) was shown in Example 2.6.2. Based on this information, draw the structural formula of dichloromethane (CH_2Cl_2).

2. What is the total number of electrons present in each ion?

a. F^-
b. Rb^+
c. Ce^{3+}
d. Zr^{4+}
e. Zn^{2+}
f. Kr^{2+}
g. B^{3+}

3. What is the total number of electrons present in each ion?

a. Ca^{2+}
b. Se^{2-}
c. In^{3+}
d. Sr^{2+}
e. As^{3+}
f. N^{3-}
g. Tl^+

4. Predict how many electrons are in each ion.

a. an oxygen ion with a –2 charge
b. a beryllium ion with a +2 charge
c. a silver ion with a +1 charge
d. a selenium ion with a +4 charge
e. an iron ion with a +2 charge
f. a chlorine ion with a –1 charge

5. Predict how many electrons are in each ion.

a. copper ion with a +2 charge

b. a molybdenum ion with a +4 charge
c. an iodine ion with a –1 charge
d. a gallium ion with a +3 charge
e. an ytterbium ion with a +3 charge
f. a scandium ion with a +3 charge

6. Predict the charge on the most common monatomic ion formed by each element.

a. chlorine
b. phosphorus
c. scandium
d. magnesium
e. arsenic
f. oxygen

7. Predict the charge on the most common monatomic ion formed by each element.

a. sodium
b. selenium
c. barium
d. rubidium
e. nitrogen
f. aluminum

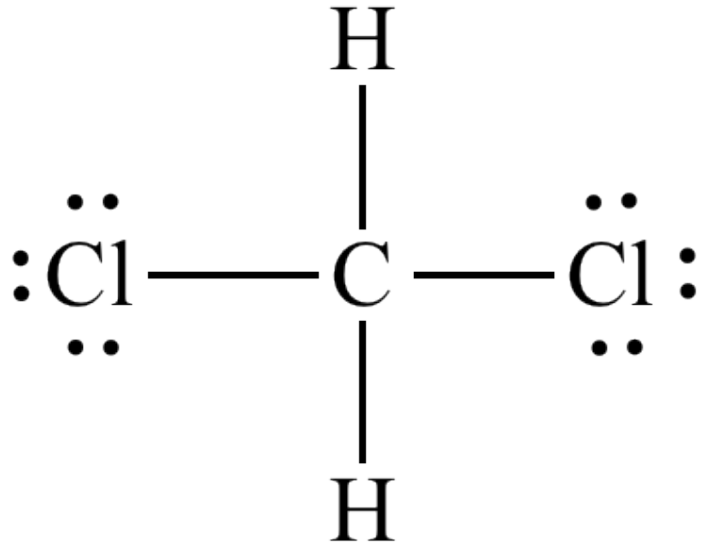
8. For each representation of a monatomic ion, identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.

a. ${}^{9}_{4}X^{2+}$
b. ${}^{1}_{1}X^{-}$
c. ${}^{16}_{8}X^{2-}$

9. For each representation of a monatomic ion, identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.

a. ${}^{7}_{3}X^{+}$
b. ${}^{19}_{9}X^{-}$
c. ${}^{27}_{13}X^{3+}$

Numerical Answers

1. 
2. Total number of electrons present in each ion:
    1. F^-
        1. 10
    2. Rb^+
        1. 36
    3. Ce^{3+}
        1. 55
    4. Zr^{4+}
        1. 36
    5. Zn^{2+}
        1. 28
    6. Kr^{2+}
        1. 34
    7. B^{3+}
        1. 2
3. Total number of electrons present in each ion:
    1. Ca^{2+}
        1. 18
    2. Se^{2-}
        1. 36
    3. In^{3+}
        1. 46
    4. Sr^{2+}
        1. 36
    5. As^{3+}
        1. 30
    6. N^{3-}
        1. 10
    7. Tl^+
        1. 80
4. How many electrons are in each ion:
    1. an oxygen ion with a –2 charge
        1. 10

2. a beryllium ion with a +2 charge
    1. 2
3. a silver ion with a +1 charge
    1. 46
4. a selenium ion with a +4 charge
    1. 30
5. an iron ion with a +2 charge
    1. 24
6. a chlorine ion with a –1 charge
    1. 18

5. How many electrons are in each ion:

    1. copper ion with a +2 charge
        1. 27
    2. a molybdenum ion with a +4 charge
        1. 38
    3. an iodine ion with a –1 charge
        1. 54
    4. a gallium ion with a +3 charge
        1. 28
    5. an ytterbium ion with a +3 charge
        1. 67
    6. a scandium ion with a +3 charge
        1. 18

6. The charge on the most common monatomic ion formed by each element:

    1. chlorine
        1. -1
    2. phosphorus
        1. -3
    3. scandium
        1. +3
    4. magnesium
        1. +2
    5. arsenic
        1. -3
    6. oxygen
        1. -2

7. The charge on the most common monatomic ion formed by each element:

    1. sodium
        1. +1
    2. selenium
        1. -2
    3. barium
        1. +2
    4. rubidium
        1. +1
    5. nitrogen
        1. +3
    6. aluminum
        1. +3
8. Identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.
    1. $^{9}_{4}X^{2+}$
        1. Parent Atom

1. Be
2. Formula of Ion
    1. Be^{2+}
3. Period and Group
    1. Period 2, Group 2

2. $^{1}_{1}X^{-}$
    1. Parent Atom
        1. H
    2. Formula of Ion
        1. H^{-}
    3. Period and Group
        1. Period 1, Group 1
3. $^{16}_{8}X^{2-}$
    1. Parent Atom
        1. O
    2. Formula of Ion
        1. O^{2-}
    3. Period and Group
        1. Period 2, Group 16

9. Identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.
    1. $^{7}_{3}X^{+}$
        1. Parent Atom
            1. Li
        2. Formula of Ion
            1. Li^{+}
        3. Period and Group
            1. Period 2, Group 1
    2. $^{19}_{9}X^{-}$
        1. Parent Atom
            1. F
        2. Formula of Ion
            1. F^{-}
        3. Period and Group
            1. Period 2, Group 17
    3. $^{27}_{13}X^{3+}$
        1. Parent Atom
            1. Al
        2. Formula of Ion
            1. Al^{3+}
        3. Period and Group
            1. Period 3, Group 13

2.7: Ions and Ionic Compounds

2.8: Naming Inorganic Compounds

Conceptual Problems

1. What are the differences and similarities between a polyatomic ion and a molecule?

2. Classify each compound as ionic or covalent.

a. $Zn_3(PO_4)_2$

b. $C_6H_5CO_2H$
c. $K_2Cr_2O_7$
d. CH_3CH_2SH
e. NH_4Br
f. CCl_2F_2

3. Classify each compound as ionic or covalent. Which are organic compounds and which are inorganic compounds?

a. $CH_3CH_2CO_2H$
b. $CaCl_2$
c. $Y(NO_3)_3$
d. H_2S
e. $NaC_2H_3O_2$

4. Generally, one cannot determine the molecular formula directly from an empirical formula. What other information is needed?

5. Give two pieces of information that we obtain from a structural formula that we cannot obtain from an empirical formula.

6. The formulas of alcohols are often written as ROH rather than as empirical formulas. For example, methanol is generally written as CH_3OH rather than CH_4O. Explain why the ROH notation is preferred.

7. The compound dimethyl sulfide has the empirical formula C_2H_6S and the structural formula CH_3SCH_3. What information do we obtain from the structural formula that we do not get from the empirical formula? Write the condensed structural formula for the compound.

8. What is the correct formula for magnesium hydroxide—$MgOH_2$ or $Mg(OH)_2$? Why?

9. Magnesium cyanide is written as $Mg(CN)_2$, not $MgCN_2$. Why?

10. Does a given hydrate always contain the same number of waters of hydration?

Conceptual Solutions

1. Polyatomic ions and molecules are similar in that both are groups of multiple atoms held together by covalent bonds. However, polyatomic ions have net electrical charges, either positive or negative, while molecules do not.

2. Classify each compound as ionic or covalent.

    1. $Zn_3(PO_4)_2$
        1. Ionic
    2. $C_6H_5CO_2H$
        1. Covalent
    3. $K_2Cr_2O_7$
        1. Ionic
    4. CH_3CH_2SH
        1. Covalent
    5. NH_4Br
        1. Covalent
    6. CCl_2F_2
        1. Covalent

3. Classify each compound as ionic or covalent, organic or inorganic.
    1. $CH_3CH_2CO_2H$
        1. Covalent, organic
    2. $CaCl_2$
        1. Ionic, inorganic
    3. $Y(NO_3)_3$
        1. Ionic, inorganic

4. H_2S
    1. Covalent, inorganic
5. $NaC_2H_3O_2$
    1. Ionic, organic

4. In order to find the molecular formula from the empirical formula, the molar mass of the compound is also needed.
5. Structural Formulas allow us to see the types of bonds connecting atoms within a molecule or ion (single, double, or triple bonds), as well as a general shape in which the atoms are arranged.
6. OH is the functional group of the alcohol family, which confers upon it its characteristic properties. By using the ROH notation, one can tell with a single glance that a compound is an alcohol.
7. The structural formula gives us the connectivity of the atoms in the molecule or ion, as well as a schematic representation of their arrangement in space. Empirical formulas tell us only the ratios of the atoms present. The condensed structural formula of dimethylsulfide is $(CH_3)_2S$.
8. The correct formula is $Mg(OH)_2$. Being a neutral molecule, the charges on the components must even out to 0 — Mg has a charge of +2, O has a charge of -2, while H has a charge of +1. $MgOH_2$ would result in a polyatomic ion with charge +2, since there would only be one O. Additionally, Hydroxide refers specifically to the diatomic anion OH^-, so Magnesium Hydroxide would need to be composed of OH^- due to the name.
9. The functional group present in cyanides is the cyano group, which is CN. The cyano group has a charge of -1. In order for the molecule to be a *Cyanide*, it must contain this functional group, and since this is a neutral molecule the charges must add up to 0. Given that Mg has a charge of +2, there must be two CN groups in order to even out the charges.
10. Yes. Each specific hydrate has a certain ratio of waters of hydration bound to it, differing between compounds (but not within the same hydrate).

Numerical Problems

1. Write the formula for each compound.

a. magnesium sulfate, which has 1 magnesium atom, 4 oxygen atoms, and 1 sulfur atom
b. ethylene glycol (antifreeze), which has 6 hydrogen atoms, 2 carbon atoms, and 2 oxygen atoms
c. acetic acid, which has 2 oxygen atoms, 2 carbon atoms, and 4 hydrogen atoms
d. potassium chlorate, which has 1 chlorine atom, 1 potassium atom, and 3 oxygen atoms
e. sodium hypochlorite pentahydrate, which has 1 chlorine atom, 1 sodium atom, 6 oxygen atoms, and 10 hydrogen atoms

2. Write the formula for each compound.

a. cadmium acetate, which has 1 cadmium atom, 4 oxygen atoms, 4 carbon atoms, and 6 hydrogen atoms
b. barium cyanide, which has 1 barium atom, 2 carbon atoms, and 2 nitrogen atoms
c. iron(III) phosphate dihydrate, which has 1 iron atom, 1 phosphorus atom, 6 oxygen atoms, and 4 hydrogen atoms
d. manganese(II) nitrate hexahydrate, which has 1 manganese atom, 12 hydrogen atoms, 12 oxygen atoms, and 2 nitrogen atoms
e. silver phosphate, which has 1 phosphorus atom, 3 silver atoms, and 4 oxygen atoms

3. Complete the following table by filling in the formula for the ionic compound formed by each cation-anion pair.

Ion	K^+	Fe^{3+}	NH_4^+	Ba^{2+}
Cl^-	KCl			
SO_4^{2-}				
PO_4^{3-}				
NO_3^-				
OH^-				

4. Write the empirical formula for the binary compound formed by the most common monatomic ions formed by each pair of elements.

a. zinc and sulfur
b. barium and iodine
c. magnesium and chlorine
d. silicon and oxygen
e. sodium and sulfur

5. Write the empirical formula for the binary compound formed by the most common monatomic ions formed by each pair of elements.

a. lithium and nitrogen
b. cesium and chlorine
c. germanium and oxygen
d. rubidium and sulfur
e. arsenic and sodium

6. Write the empirical formula for each compound.

a. $Na_2S_2O_4$
b. B_2H_6
c. $C_6H_{12}O_6$
d. P_4O_{10}
e. $KMnO_4$

7. Write the empirical formula for each compound.

a. Al_2Cl_6
b. $K_2Cr_2O_7$
c. C_2H_4
d. $(NH_2)_2CNH$
e. CH_3COOH

Numerical Answers

1. Formula of each compound:
    1. magnesium sulfate
        1. $MgSO_4$
    2. ethylene glycol (antifreeze)
        1. $(CH_2OH)_2$
    3. acetic acid
        1. CH_3COOH
    4. potassium chlorate
        1. $KClO_3$
    5. sodium hypochlorite pentahydrate
        1. $NaOCl{\cdot}5H_2O$
2. Formula of each compound:
    1. cadmium acetate, which has 1 cadmium atom, 4 oxygen atoms, 4 carbon atoms, and 6 hydrogen atoms
        1. $Cd(O_2CCH_3)_2$
    2. barium cyanide, which has 1 barium atom, 2 carbon atoms, and 2 nitrogen atoms
        1. $Ba(CN)_2$
    3. iron(III) phosphate dihydrate, which has 1 iron atom, 1 phosphorus atom, 6 oxygen atoms, and 4 hydrogen atoms
        1. $FePO_4 \cdot 2H_2O$
    4. manganese(II) nitrate hexahydrate, which has 1 manganese atom, 12 hydrogen atoms, 12 oxygen atoms, and 2 nitrogen atoms
        1. $Mn(NO_3)_2 \cdot 6H_2O$
    5. silver phosphate, which has 1 phosphorus atom, 3 silver atoms, and 4 oxygen atoms
        1. Ag_3PO_4

3.

Ion	K^+	Fe^{3+}	NH_4^+	Ba^{2+}
Cl^-	KCl	$FeCl_3$	NH_4Cl	$BaCl_2$
SO_4^{2-}	K_2SO_4	Fe2(SO4)3	$(NH_4)_2SO_4$	$BaSO_4$
$PO_4\ 3^-$	K_3PO_4	$FePO_4$	$(NH_4)3PO_4$	$Ba3(PO_4)_2$
NO_3^-	KNO_3	$Fe(NO3)_3$	$NH4NO_3$	$Ba(NO_3)_2$
OH^-	KOH	$Fe(OH)_3$	NH_4OH	$Ba(OH)_2$

4. The empirical formula for the binary compound:
    1. zinc and sulfur
        1. ZnS
    2. barium and iodine
        1. BaI_2
    3. magnesium and chlorine
        1. $MgCl_2$
    4. silicon and oxygen
        1. SiO_2
    5. sodium and sulfur
        1. Na_2S
5. The empirical formula for the binary compound:
    1. lithium and nitrogen
        1. Li_3N
    2. cesium and chlorine
        1. CsCl
    3. germanium and oxygen
        1. GeO_2
    4. rubidium and sulfur
        1. Rb_2S
    5. arsenic and sodium
        1. Na_3As

6. The empirical formula for each compound:

    1. $Na_2S_2O_4$
        1. $NaSO_2$
    2. B_2H_6
        1. BH_3
    3. $C_6H_{12}O_6$
        1. CH_2O
    4. P_4O_{10}
        1. P_2O_5
    5. $KMnO_4$
        1. $KMnO_4$
7. The empirical formula for each compound:
    1. Al_2Cl_6
        1. $AlCl_3$
    2. $K_2Cr_2O_7$
        1. $K_2Cr_2O_7$
    3. C_2H_4
        1. CH_2
    4. $(NH_2)_2CNH$
        1. CH_5N_3

5. CH_3COOH
    1. CH_2O

2.9: Some Simple Organic Compounds

Conceptual Problems

1. Benzene (C_6H_6) is an organic compound, and KCl is an ionic compound. The sum of the masses of the atoms in each empirical formula is approximately the same. How would you expect the two to compare with regard to each of the following? What species are present in benzene vapor?

a. melting point
b. type of bonding
c. rate of evaporation
d. structure

2. Can an inorganic compound be classified as a hydrocarbon? Why or why not?

3. Is the compound $NaHCO_3$ a hydrocarbon? Why or why not?

4. Name each compound.

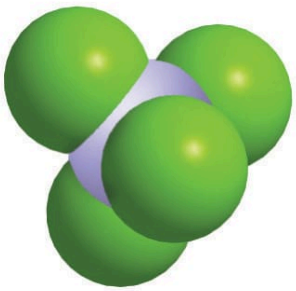
a. NiO
b. TiO_2
c. N_2O
d. CS_2
e. SO_3
f. NF_3
g. SF_6

5. Name each compound.

a. $HgCl_2$
b. IF_5
c. N_2O_5
d. Cl_2O
e. HgS
f. PCl_5

6. For each structural formula, write the condensed formula and the name of the compound.

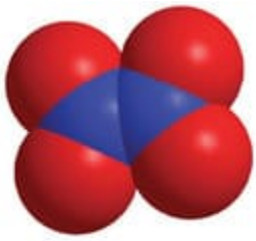
a.



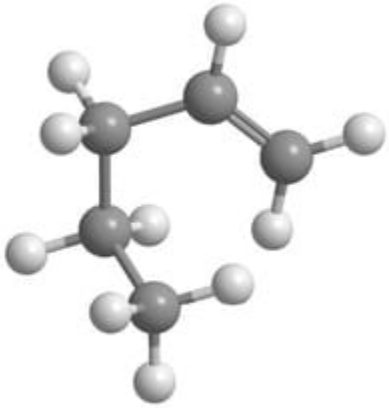
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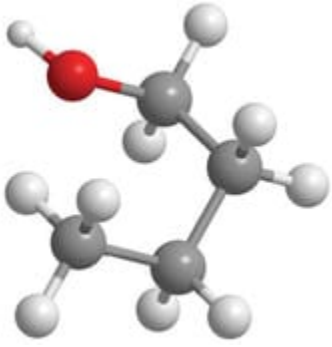
c.



d.



e.



7. For each structural formula, write the condensed formula and the name of the compound.

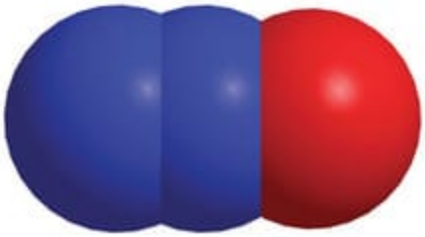
a.



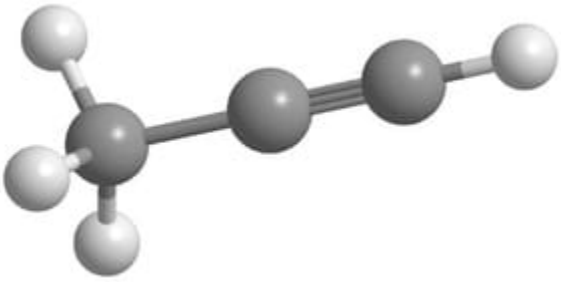
b.



c.



d.



8. Would you expect PCl_3 to be an ionic compound or a covalent compound? Explain your reasoning.

9. What distinguishes an aromatic hydrocarbon from an aliphatic hydrocarbon?

10. The following general formulas represent specific classes of hydrocarbons. Refer to Table 2.7 "The First 10 Straight-Chain Alkanes" and Table 2.8 "Some Common Acids That Do Not Contain Oxygen" and Figure 2.16 and identify the classes.

a. $C_nH_{2n + 2}$
   1.
b. C_nH_{2n}
   1.
c. $C_nH_{2n - 2}$

1.

11. Using R to represent an alkyl or aryl group, show the general structure of an

a. alcohol.
b. phenol.

Conceptual Answer

1.

	Benzene	KCl
Melting Point	Lower	Higher
Type of Bonding	Covalent	Ionic
Rate of Evaporation	Higher	Lower
Structure	Planar Molecule	Ionic Crystal

2. An inorganic compound cannot be classified as a hydrocarbon, as hydrocarbons are by definition organic.
3. $NaHCO_3$ is not a hydrocarbon. Hydrocarbons consist entirely of carbon and hydrogen atoms, while $NaHCO_3$ also contains nitrogen and oxygen.
4. Name each compound.
    1. NiO
        1. Nickel Oxide
    2. TiO_2
        1. Titanium Dioxide
    3. N_2O
        1. Nitrous Oxide
    4. CS_2
        1. Carbon Disulfide
    5. SO_3
        1. Sulfur Trioxide
    6. NF_3
        1. Nitrogen Trifluoride
    7. SF_6
        1. Sulfur Hexafluoride
5. Name each compound.
    1. $HgCl_2$
        1. Mercury(II) Chloride
    2. IF_5
        1. Iodine Pentafluoride
    3. N_2O_5
        1. Dinitrogen Pentoxide
    4. Cl_2O
        1. Dichlorine Monoxide
    5. HgS
        1. Mercury(II) Sulfide
    6. PCl_5
        1. Phosphorus Pentachloride
6.
7.
8. PCl_3 would be expected to be a covalent compound. The electronegativity difference between P and Cl is not great enough to create an ionic bond.
9. An aromatic hydrocarbon contains a conjugated ring system (in other words, a ring system composed of alternating single and double bonds). An aliphatic hydrocarbon, on the other hand, can be linear, or it can contain a *non*-conjugated ring system.
10. Identify the classes.
    1. C_nH_{2n+2}

    1. Alkane
2. C_nH_{2n}
    1. Alkene
3. C_nH_{2n-2}
    1. Alkyne

11.

1. ROH, where R is an alkyl group, in other words an alkane where one hydrogen is removed. The OH is attached to a saturated carbon atom.
2. ROH, where R is an aryl group, in other words an aromatic ring where one hydrogen is removed. The OH is attached directly to the ring.

Numerical Problems

1. Write the formula for each compound.

a. dinitrogen monoxide
b. silicon tetrafluoride
c. boron trichloride
d. nitrogen trifluoride
e. phosphorus tribromide

2. Write the formula for each compound.

a. dinitrogen trioxide
b. iodine pentafluoride
c. boron tribromide
d. oxygen difluoride
e. arsenic trichloride

3. Write the formula for each compound.

a. thallium(I) selenide
b. neptunium(IV) oxide
c. iron(II) sulfide
d. copper(I) cyanide
e. nitrogen trichloride

4. Name each compound.

a. RuO_4
b. PbO_2
c. MoF_6
d. $Hg_2(NO_3)_2{\cdot}2H_2O$
e. WCl_4

5. Name each compound.

a. NbO_2
b. MoS2
c. P_4S_{10}
d. Cu_2O
e. ReF_5

6. Draw the structure of each compound.

a. propyne
b. ethanol
c. n-hexane

d. cyclopropane
e. benzene

7. Draw the structure of each compound.

a. 1-butene
b. 2-pentyne
c. cycloheptane
d. toluene
e. phenol

Numerical Answers

1.
    1. N_2O
    2. SiF_4
    3. BCl_3
    4. NF_3
    5. PBr_3
2.
    1. N_2O_3
    2. IF_5
    3. BBr_3
    4. OF_2
    5. $AsCl_3$
3.
    1. TlSe
    2. NpO_2
    3. FeS
    4. CuCN
    5. NCl_3
4.
    1. Ruthenium Tetroxide
    2. Lead Dioxide (or Lead(IV) Oxide)
    3. Molybdenum Hexafluoride (or Molybdenum(VI) Fluoride)
    4. Mercury(I) Nitrate Dihydrate
    5. Tungsten Tetrachloride (or Tungsten(IV) Chloride)

5.

a. niobium (IV) oxide
b. molybdenum (IV) sulfide
c. tetraphosphorus decasulfide
d. copper(I) oxide
e. rhenium(V) fluoride

6.

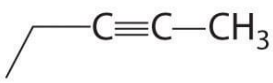
1. ChemSpider 2D Image | Propyne | C3H4
2. ChemSpider 2D Image | Ethanol | C2H6O
3. ChemSpider 2D Image | Hexane | C6H14
4. ChemSpider 2D Image | Cyclopropane | C3H6
5. ChemSpider 2D Image | Benzene | C6H6

7.

a.



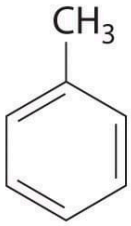
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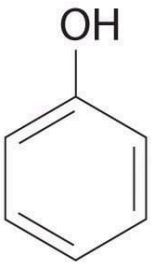
c.



d.



e.



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2.S: Atoms, Molecules, and Ions (Summary)

This chapter introduced some of the fundamental concepts of chemistry, with particular attention to the basic properties of atoms and elements. These entities are the building blocks of all substances we encounter, yet most common substances do not consist of only pure elements or individual atoms. Instead, nearly all substances are chemical compounds or mixtures of chemical compounds. Although there are only about 115 elements (of which about 86 occur naturally), millions of chemical compounds are known, with a tremendous range of physical and chemical properties. Consequently, a major emphasis of modern chemistry focuses on understanding the relationship between the structures and properties of chemical compounds.

2.1: The Atomic Theory of Matter

- Dalton's atomic theory of matter:
  1. Each element is composed of extremely small particles called atoms
  2. All atoms of a given element are identical; the atoms of different elements are different and have different properties
  3. Atoms of an element are not changed into different types of atoms by chemical reactions
  4. Compounds are formed when atoms of more than one element combine
- explains the law of constant composition, law of conservation of mass

2.2: The Discovery of Atomic Structure

- subatomic particles – what atoms are composed of
- Like charges repel each other; unlike charges attract

Cathode Rays and Electrons

- cathode rays – radiation resulting from a high voltage
- cause certain materials to give off light (fluoresce)
- mass of an electron $9.10939*10^{-28}$g
- 2000 times smaller than hydrogen

1.2.2 Radioactivity

- radioactivity – spontaneous emission of radiation
- three types of radiation: alpha (a), beta (b), gamma (g)
- alpha and beta radiation are affected by an electric field
- beta particles have a charge of 1-
- alpha particles have a charge of 2+
- gamma radiation has no particles and no charge

1.2.3 The Nuclear Atom

- Rutherford determined that there was a nucleus in every atom
- Protons discovered by Rutherford in 1919
- Neutrons discovered by James Chadwich in 1932

2.3: The Modern View of Atomic Structure

- charge of an electron is $-1.602*10^{-19}$
- charge of a proton is $+1.602*10^{-19}$
- $1.602*10^{-19}$ is called to electronic charge

Particle, Charge and Mass (amu)

Particle	Charge	Mass (amu)
Proton	Positive	1.0073
Neutron	None	1.0087
Electron	Negative	$5.486*10^{-4}$

- atomic mass unit (amu) – equals $1.66054*10^{-24}$ grams
- angstrom (Å) – unit of length to measure atomic dimensions
  - 1 angstrom = 10^{-10}m
- atoms have diameters of 1-5 Å
- nucleus – diameter of 10^{-4} Å

2.4: Atomic Mass

- all atoms of an element have the same number of protons in the nucleus
- isotopes - atoms of the same element that have a different number of neutrons
- atomic number – the number of protons in an atom
- mass number – number of protons + number of neutrons
- nuclide – atom of a specific isotope

2.5: The Periodic Table

- periodic table – the arrangement of all the elements by atomic number and similarities into a table
- columns = groups
- metallic elements – all elements on the left side and in the middle of the periodic table
- nonmetallic elements – elements on the periodic table that are divided by a diagonal steplike line from boron to astatine
- metalloids – properties of metals and nonmetals

2.6: Molecules and Molecular Compounds

- molecule – two or more atoms bonded together

1. Molecules and Chemical Formulas

- ◦ chemical formula – way of representing molecules
  ◦ diatomic molecule – any molecule made up of two atoms
  ◦ molecular compounds – contains more than one type of atom

1. Molecular and Empirical Formulas

- ◦ molecular formulas – chemical formulas that indication the actual number of atoms

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- ◦ empirical formula – chemical formulas that only give the relative number of atoms

1. 1. 1. Picturing Molecules

- ◦ [Original Image Removed] structural formulas – shows which atoms are attached to other atoms
- ◦ [Original Image Removed] perspective drawing – gives an idea of the three-dimensional shape of a molecule

- ◦ [Original Image Removed] ball-and-stick models – shows atoms as balls bonded by sticks
- ◦ space-filling model – accurate representation of what atoms would look like

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2.7: Ions and Ionic Compounds

- ion – charged particle formed by the removal or addition of an electron
- cation – ion with a positive charge
- anion – ion with a negative charge
- metal atoms tend to lose electrons
- nonmetal atoms tend to gain electrons
- polyatomic ions – joined atoms that have a net positive or negative charge

1. Predicting Ionic Charges

- ◦ alkalie metals form 1+ ions
  ◦ alkaline earth from 2+ ions
  ◦ halogens form 1- ions
  ◦ group 6A from 2- ions

1. Ionic Compounds

- ◦ ionic compound – a compound that contains positively and negatively charged ions
  ◦ ionic compounds are generally combinations of metals and nonmetals
  ◦ molecular compounds are generally nonmetals only

2.8: Naming Inorganic Compounds

- chemical nomenclature – the naming of substances
- over 10 million known chemical substances
- organic compounds – contain carbon
- inorganic compounds – everything else

- **positive ions**

a. a. cations formed from atoms have the same name as the metal
   b. if a metal can form cations of differing charges, the positive charge is given by a roman numeral in parentheses following the name of the metal
   c. cations formed from nonmetal atoms have names that end in –ium

- **Negative Ions**

- monatomic anions have names formed by dropping the ending of the name of the element and adding the ending –ide
- polyatomic anions containing oxygen have names ending in –ate or –ite
  ◦ called oxyanions

a. a. anions derived by adding H^+ to an oxyanion are named by adding as a prefix the word hydrogen or dihydrogen, as appropriate

1. 1. Ionic compounds

a. a. names of ionic compounds are the cation name followed by the anion name

1. 1. 1. Names and formulas of Acids

1. 1. acids bases on anions whose names end in –ide have associated acids that have the hydro- prefix and an –ic ending

2. acids based on anions whose names end in –ate or -ite

Anion and Acid Fill in the Blanks

Anion	Acid
___ide	Hydro___ic acid
___ate	____ic acid
___ite	____ous acid

1. Names and Formulas of Binary Molecular Compounds

- the name of the element farthest to the left in the periodic table is usually written first
- if elements in same group lower one written first
- name of second element is given an –ide ending
- greek prefixes used to indicate number of atoms of each element
- if prefix ends in a or o and the name of the anion begins with a vowel, the a or o is dropped

Prefixs and Meanings

Prefix	Meaning
Mono-	1
Di-	2
Tri-	3
Tetra-	4
Penta-	5
Hexa-	6
Hepta-	7
Octa-	8
Nona-	9
Deca-	10

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3: STOICHIOMETRY- CHEMICAL FORMULAS AND EQUATIONS

Stoichiometry is the calculation of relative quantities of reactants and products in chemical reactions. Stoichiometry is founded on the **law of conservation of mass** where the total mass of the reactants equals the total mass of the products leading to the insight that the relations among quantities of reactants and products typically form a ratio of positive integers. This means that if the amounts of the separate reactants are known, then the amount of the product can be calculated. Conversely, if one reactant has a known quantity and the quantity of product can be empirically determined, then the amount of the other reactants can also be calculated.

We begin this chapter by describing the relationship between the mass of a sample of a substance and its composition. We then develop methods for determining the quantities of compounds produced or consumed in chemical reactions, and we describe some fundamental types of chemical reactions. By applying the concepts and skills introduced in this chapter, you will be able to explain what happens to the sugar in a candy bar you eat, what reaction occurs in a battery when you start your car, what may be causing the “ozone hole” over Antarctica, and how we might prevent the hole’s growth.

3.1: Chemical Equations

3.2: Some Simple Patterns of Chemical Reactivity

3.3: Formula Masses

3.4: Avogadro's Number and the Mole

3.5: Empirical Formulas from Analysis

3.6: Quantitative Information from Balanced Equations

3.7: Limiting Reactants

3.E: Stoichiometry (Exercises)

3.S: Stoichiometry (Summary)

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3.1: Chemical Equations

Learning Objectives

- To describe a chemical reaction.
- To calculate the quantities of compounds produced or consumed in a chemical reaction

What happens to matter when it undergoes chemical changes? The Law of conservation of mass says that "***Atoms are neither created, nor destroyed, during any chemical reaction***." Thus, the same collection of atoms is present after a reaction as before the reaction. The changes that occur during a reaction just involve the *rearrangement* of atoms. In this section we will discuss ***stoichiometry*** (the "measurement of elements").

Chemical Equations

As shown in Figure 3.1.1, applying a small amount of heat to a pile of orange ammonium dichromate powder results in a vigorous reaction known as the ammonium dichromate volcano. Heat, light, and gas are produced as a large pile of fluffy green chromium(III) oxide forms. This reaction is described with a chemical equation, an expression that gives the identities and quantities of the substances in a chemical reaction.



Figure 3.1.1: An Ammonium Dichromate Volcano: Change during a Chemical Reaction. The starting material is solid ammonium dichromate. A chemical reaction transforms it to solid chromium(III) oxide, depicted showing a portion of its chained structure, nitrogen gas, and water vapor (in addition, energy in the form of heat and light is released). During the reaction, the distribution of atoms changes, but the number of atoms of each element does not change. Because the numbers of each type of atom are the same in the reactants and the products, the chemical equation is balanced. (CC BY-SA 3.0; Mikk Mihkel Vaabel via Wikipedia). See video here: www.youtube.com/watch?v=CW4hN0dYnkM

Chemical reactions are represented on paper by ***chemical equations***. For example, hydrogen gas (H_2) can react (burn) with oxygen gas (O_2) to form water (H_2O). The *chemical equation* for this *reaction* is written as:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

Chemical formulas and other symbols are used to indicate the starting materials, or reactants, which by convention are written on the left side of the equation, and the final compounds, or products, which are written on the right. An arrow points from the reactant to the products. The chemical reaction for the ammonium dichromate volcano in Figure 3.1.1 is

$$\underbrace{(NH_4)_2Cr_2O_7}_{reactant} \rightarrow \underbrace{Cr_2O_3 + N_2 + 4\,H_2O}_{products} \tag{3.1.1}$$

The arrow is read as “yields” or “reacts to form.” Equation 3.1.1 indicates that ammonium dichromate (the reactant) yields chromium(III) oxide, nitrogen, and water (the products). The equation for this reaction is even more informative when written as follows:

$$(\mathrm{NH_4})_2\mathrm{Cr_2O_7\,(s)} \rightarrow \mathrm{Cr_2O_3\,(s)} + \mathrm{N_2\,(g)} + 4\,\mathrm{H_2O\,(g)} \tag{3.1.2}$$

Equation 3.1.2 is identical to Equation 3.1.1 except for the addition of abbreviations in parentheses to indicate the physical state of each species. The abbreviations are (s) for solid, (l) for liquid, (g) for gas, and (aq) for an aqueous solution, a solution of the substance in water.

Consistent with the law of conservation of mass, the numbers of each type of atom are the same on both sides of Equations 3.1.1 and 3.1.2. Each side of the reaction has two chromium atoms, seven oxygen atoms, two nitrogen atoms, and eight hydrogen atoms.

In a balanced chemical equation, both the numbers of each type of atom and the total charge are the same on both sides. Equations 3.1.1 and 3.1.2 are balanced chemical equations. What is different on each side of the equation is how the atoms are arranged to make molecules or ions. A chemical reaction represents a change in the distribution of atoms, but not in the number of atoms. In this reaction, and in most chemical reactions, bonds are broken in the reactants (here, Cr–O and N–H bonds), and new bonds are formed to create the products (here, O–H and N≡N bonds). If the numbers of each type of atom are different on the two sides of a chemical equation, then the equation is unbalanced, and it cannot correctly describe what happens during the reaction. To proceed, the equation must first be balanced.

A chemical reaction changes only the distribution of atoms, not the number of atoms.

YouTube Video

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Introduction to Chemical Reaction Equations: Introduction to Chemical Reaction Equations, YouTube(opens in new window) [youtu.be]

Balancing Simple Chemical Equations

When a chemist encounters a new reaction, it does not usually come with a label that shows the balanced chemical equation. Instead, the chemist must identify the reactants and products and then write them in the form of a chemical equation that may or may not be balanced as first written. Consider, for example, the combustion of n-heptane (C_7H_{16}), an important component of gasoline:

$$\mathrm{C_7H_{16}\,(l)} + \mathrm{O_2\,(g)} \rightarrow \mathrm{CO_2\,(g)} + \mathrm{H_2O\,(g)} \tag{3.1.3}$$

The complete combustion of any hydrocarbon with sufficient oxygen always yields carbon dioxide and water.



Figure 3.1.2: An Example of a Combustion Reaction. The wax in a candle is a high-molecular-mass hydrocarbon, which produces gaseous carbon dioxide and water vapor in a combustion reaction (Equation 3.1.3).

Equation 3.1.3 is not balanced: the numbers of each type of atom on the reactant side of the equation (7 carbon atoms, 16 hydrogen atoms, and 2 oxygen atoms) is not the same as the numbers of each type of atom on the product side (1 carbon atom, 2 hydrogen atoms, and 3 oxygen atoms). Consequently, the coefficients of the reactants and products must be adjusted to give the same numbers of atoms of each type on both sides of the equation. Because the identities of the reactants and products are fixed, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure 3.1.3.

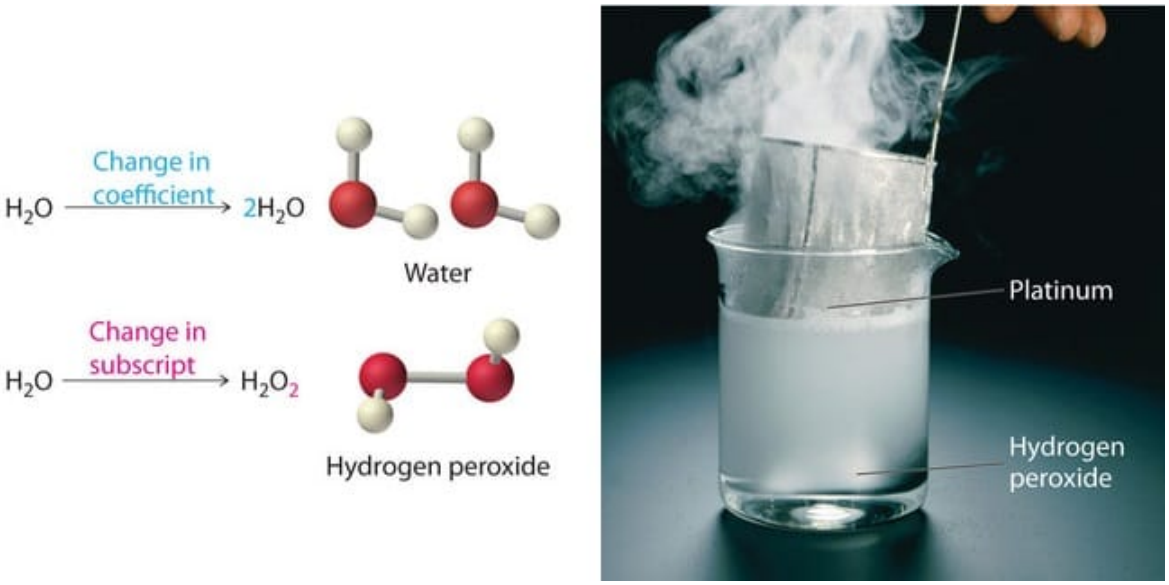


Figure 3.1.3: Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances. H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.

Left: Example of changing coefficients or subscripts. Right: Platinum dissolving in hydrogen peroxide.

YouTube Video

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Balancing Combustion Reactions: Balancing Combustions Reactions, YouTube(opens in new window) [youtu.be]

The simplest and most generally useful method for balancing chemical equations is “inspection,” better known as trial and error. The following is an efficient approach to balancing a chemical equation using this method.

Steps in Balancing a Chemical Equation

1. Identify the most complex substance.
2. Beginning with that substance, choose an element that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element on both sides.
3. Balance polyatomic ions (if present) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.
5. Check your work by counting the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

Example 3.1.1A: Combustion of Heptane

To demonstrate this approach, let’s use the combustion of n-heptane (Equation 3.1.3) as an example.

1. **Identify the most complex substance**. The most complex substance is the one with the largest number of different atoms, which is $\mathrm{C_7H_{16}}$. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients**. Try to adjust the coefficients of the molecules on the other side of the equation to obtain the same numbers of atoms on both sides. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which contains 1 carbon atom, on the right side:

$$\mathrm{C_7H_{16} + O_2 \rightarrow 7\,CO_2 + H_2O} \tag{3.1.4}$$

3. **Balance polyatomic ions as a unit**. There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms**. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H2O molecules, each of which contains 2 hydrogen atoms, on the right side:

$$\mathrm{C_7H_{16} + O_2 \rightarrow 7\,CO_2 + 8\,H_2O} \tag{3.1.5}$$

The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O_2, on the reactant side:

$$\mathrm{C_7H_{16}\,(l) + 11\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g)} \tag{3.1.6}$$

5. **Check your work**. The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. Always check to be sure that a chemical equation is balanced.The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start.

Example 3.1.1B: Combustion of Isooctane

Consider, for example, a similar reaction, the combustion of isooctane ($\mathrm{C_8H_{18}}$). Because the combustion of any hydrocarbon with oxygen produces carbon dioxide and water, the unbalanced chemical equation is as follows:

$$\mathrm{C_8H_{18}\,(l) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g)} \tag{3.1.7}$$

1. **Identify the most complex substance**. Begin the balancing process by assuming that the final balanced chemical equation contains a single molecule of isooctane.

2. **Adjust the coefficients**. The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that there must be 8 CO_2 molecules in the products:

$$\mathrm{C_8H_{18} + O_2 \rightarrow 8\,CO_2 + H_2O} \tag{3.1.8}$$

3. **Balance polyatomic ions as a unit**. This step does not apply to this equation.
4. **Balance the remaining atoms**. Eighteen hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products:

$$\mathrm{C_8H_{18} + O_2 \rightarrow 8\,CO_2 + 9\,H_2O} \tag{3.1.9}$$

The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 molecule, we must use a fractional coefficient (25/2) to balance the oxygen atoms:

$$\mathrm{C_8H_{18} + \tfrac{25}{2}\,O_2 \rightarrow 8\,CO_2 + 9\,H_2O} \tag{3.1.10}$$

Equation 3.1.10 is now balanced, but we usually write equations with whole-number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by 2:

$$\mathrm{2\,C_8H_{18}\,(l) + 25\,O_2\,(g) \rightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g)} \tag{3.1.11}$$

5. **Check your work**. The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side.

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Balancing Complex Chemical Equations: Balancing Complex Chemical Equations, YouTube(opens in new window) [youtu.be]

Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

Example 3.1.1C: Hydroxyapatite

The reaction of the mineral hydroxyapatite ($\mathrm{Ca_5(PO_4)_3(OH)}$) with phosphoric acid and water gives $\mathrm{Ca(H_2PO_4)_2 \cdot H_2O}$ (calcium dihydrogen phosphate monohydrate). Write and balance the equation for this reaction.



Hydroxyapatite (Extra close brace or missing open brace) crystal

Given: reactants and product

Asked for: balanced chemical equation

Strategy:

A. Identify the product and the reactants and then write the unbalanced chemical equation.
B. Follow the steps for balancing a chemical equation.

Solution:

A We must first identify the product and reactants and write an equation for the reaction. The formulas for hydroxyapatite and calcium dihydrogen phosphate monohydrate are given in the problem (recall that phosphoric acid is H_3PO_4). The initial (unbalanced) equation is as follows:

$$\mathrm{Ca_5(PO_4)_3(OH)\,(s) + H_3PO_4\,(aq) + H_2O_{(l)} \rightarrow Ca(H_2PO_4)_2 \cdot H_2O_{(s)}}$$

1. **B Identify the most complex substance**. We start by assuming that only one molecule or formula unit of the most complex substance, $\mathrm{Ca_5(PO_4)_3(OH)}$, appears in the balanced chemical equation.

2. **Adjust the coefficients**. Because calcium is present in only one reactant and one product, we begin with it. One formula unit of $\mathrm{Ca_5(PO_4)_3(OH)}$ contains 5 calcium atoms, so we need 5 $Ca(H_2PO_4)_2 \bullet H_2O$ on the right side:

$$\mathrm{Ca_5(PO_4)_3(OH) + H_3PO_4 + H_2O \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O}$$

3. **Balance polyatomic ions as a unit**. It is usually easier to balance an equation if we recognize that certain combinations of atoms occur on both sides. In this equation, the polyatomic phosphate ion (PO_4^{3-}), shows up in three places. In H_3PO_4, the phosphate ion is combined with three H^+ ions to make phosphoric acid (H_3PO_4), whereas in $Ca(H_2PO_4)_2 \bullet H_2O$ it is combined with two H^+ ions to give the dihydrogen phosphate ion. Thus it is easier to balance PO_4 as a unit rather than counting individual phosphorus and oxygen atoms. There are 10 PO_4 units on the right side but only 4 on the left. The simplest way to balance the PO_4 units is to place a coefficient of 7 in front of H_3PO_4:

$$\mathrm{Ca_5(PO_4)_3(OH) + 7\,H_3PO_4 + H_2O \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O}$$

Although OH^- is also a polyatomic ion, it does not appear on both sides of the equation. So oxygen and hydrogen must be balanced separately.

4. **Balance the remaining atoms**. We now have 30 hydrogen atoms on the right side but only 24 on the left. We can balance the hydrogen atoms using the least complex substance, H_2O, by placing a coefficient of 4 in front of H_2O on the left side, giving a total of 4 H_2O molecules:

$$\mathrm{Ca_5(PO_4)_3(OH)\,(s) + 7\,H_3PO_4\,(aq) + 4\,H_2O\,(l) \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O\,(s)}$$

The equation is now balanced. Even though we have not explicitly balanced the oxygen atoms, there are 41 oxygen atoms on each side.

5. **Check your work**. Both sides of the equation contain 5 calcium atoms, 10 phosphorus atoms, 30 hydrogen atoms, and 41 oxygen atoms.

Exercise 3.1.1: Fermentation

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose are converted to ethanol (CH_3CH_2OH and carbon dioxide CO_2. Write a balanced chemical reaction for the fermentation of glucose.



Commercial use of fermentation. *(a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.*

Answer available at the end of this section.

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Balancing Reactions Which Contain Polyatomics: Balancing Reactions Which Contain Polyatomics, YouTube(opens in new window) [youtu.be]

Interpreting Chemical Equations

In addition to providing qualitative information about the identities and physical states of the reactants and products, a balanced chemical equation provides quantitative information. Specifically, it gives the relative amounts of reactants and products consumed or produced in a reaction. The number of atoms, molecules, or formula units of a reactant or a product in a balanced chemical equation is the coefficient of that species (e.g., the 4 preceding H_2O in Equation 3.1.1). When no coefficient is written in front of a species, the coefficient is assumed to be 1. As illustrated in Figure 3.1.4, the coefficients allow Equation 3.1.1 to be interpreted in any of the following ways:

- Two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion yield 1 formula unit of Cr_2O_3, 1 N_2 molecule, and 4 H_2O molecules.
- One mole of $(NH_4)_2Cr_2O_7$ yields 1 mol of Cr_2O_3, 1 mol of N_2, and 4 mol of H_2O.
- A mass of 252 g of $(NH_4)_2Cr_2O_7$ yields 152 g of Cr_2O_3, 28 g of N_2, and 72 g of H_2O.
- A total of 6.022×10^{23} formula units of $(NH_4)_2Cr_2O_7$ yields 6.022×10^{23} formula units of Cr_2O_3, 6.022×10^{23} molecules of N_2, and 24.09×10^{23} molecules of H_2O.

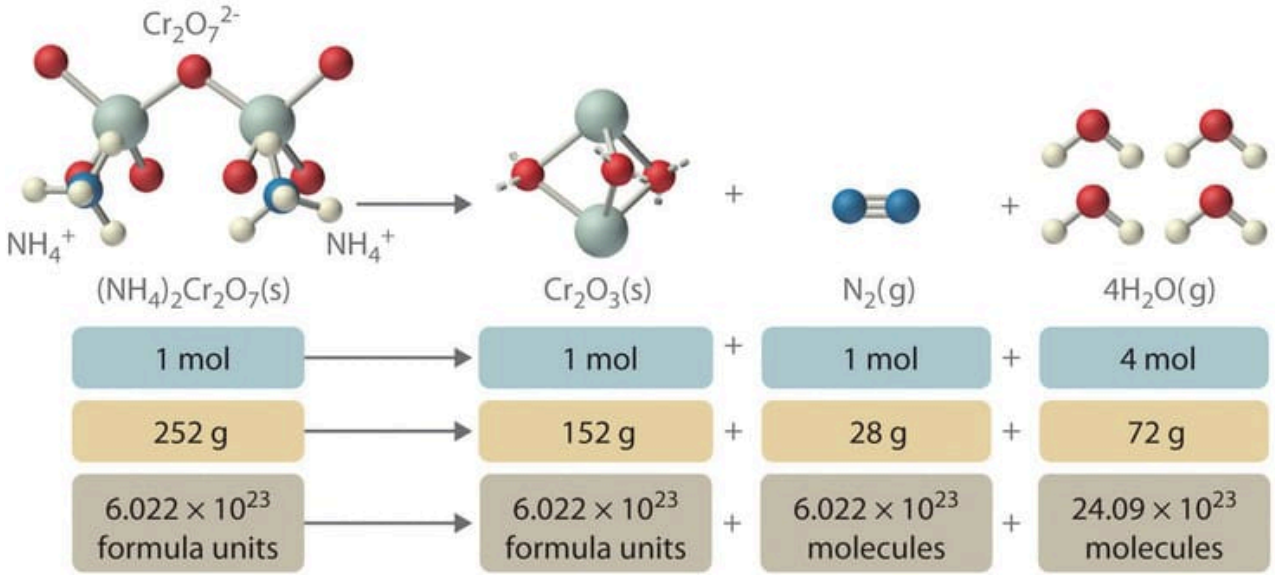


Figure 3.1.4: The Relationships among Moles, Masses, and Formula Units of Compounds in the Balanced Chemical Reaction for the Ammonium Dichromate Volcano

Chemical equation: (N H 4) 2 C r 2 O 7 dissociates into C r 2 O 3, N 2, and H 2 O. Conversions are given between moles, mass, and molecules.

These are all chemically equivalent ways of stating the information given in the balanced chemical equation, using the concepts of the mole, molar or formula mass, and Avogadro's number. The ratio of the number of moles of one substance to the number of moles of another is called the mole ratio. For example, the mole ratio of H_2O to N_2 in Equation 3.1.1 is 4:1. The total mass of reactants equals the total mass of products, as predicted by Dalton's law of conservation of mass:

$$252\ g \text{ of } (\mathrm{NH_4})_2\mathrm{Cr_2O_7}$$

yield

$$152 + 28 + 72 = 252\ g \text{ of products.}$$

The chemical equation does not, however, show the rate of the reaction (rapidly, slowly, or not at all) or whether energy in the form of heat or light is given off. These issues are considered in more detail in later chapters.

An important chemical reaction was analyzed by Antoine Lavoisier, an 18th-century French chemist, who was interested in the chemistry of living organisms as well as simple chemical systems. In a classic series of experiments, he measured the carbon dioxide and heat produced by a guinea pig during respiration, in which organic compounds are used as fuel to produce energy, carbon dioxide, and water. Lavoisier found that the ratio of heat produced to carbon dioxide exhaled was similar to the ratio observed for the reaction of charcoal with oxygen in the air to produce carbon dioxide—a process chemists call combustion. Based on these experiments, he proposed that "Respiration is a combustion, slow it is true, but otherwise perfectly similar to that of charcoal." Lavoisier was correct, although the organic compounds consumed in respiration are substantially different from those found in charcoal. One of the most important fuels in the human body is glucose ($C_6H_{12}O_6$), which is virtually the only fuel used in the brain. Thus combustion and respiration are examples of chemical reactions.

Example 3.1.2: Combustion of Glucose

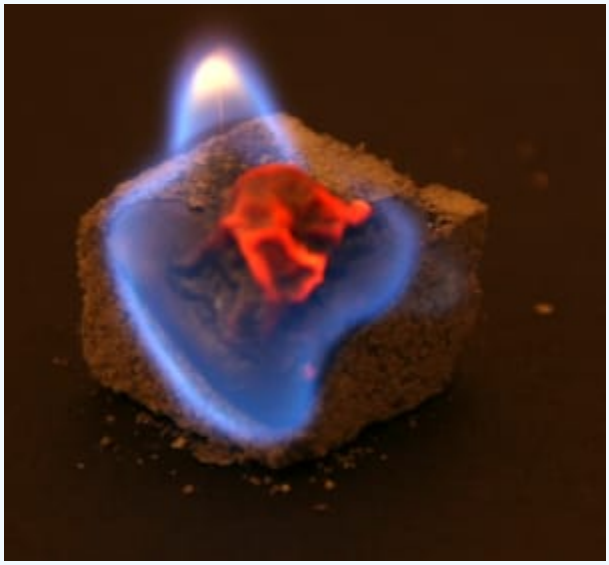
The balanced chemical equation for the combustion of glucose in the laboratory (or in the brain) is as follows:

$$\mathrm{C_6H_{12}O_6\,(s) + 6\,O_2\,(g) \rightarrow 6\,CO_2\,(g) + 6\,H_2O\,(l)}$$

Construct a table showing how to interpret the information in this equation in terms of

a. a single molecule of glucose.
b. moles of reactants and products.
c. grams of reactants and products represented by 1 mol of glucose.

d. numbers of molecules of reactants and products represented by 1 mol of glucose.



The combustion of a sugar cube consisting of sucrose with a similar reaction to the combustion of glucose. from Wikipedia.

Given: balanced chemical equation

Asked for: molecule, mole, and mass relationships

Strategy:

A. Use the coefficients from the balanced chemical equation to determine both the molecular and mole ratios.
B. Use the molar masses of the reactants and products to convert from moles to grams.
C. Use Avogadro's number to convert from moles to the number of molecules.

Solution:

This equation is balanced as written: each side has 6 carbon atoms, 18 oxygen atoms, and 12 hydrogen atoms. We can therefore use the coefficients directly to obtain the desired information.

a. One molecule of glucose reacts with 6 molecules of O_2 to yield 6 molecules of CO_2 and 6 molecules of H_2O.
b. One mole of glucose reacts with 6 mol of O_2 to yield 6 mol of CO_2 and 6 mol of H_2O.
c. To interpret the equation in terms of masses of reactants and products, we need their molar masses and the mole ratios from part b. The molar masses in grams per mole are as follows: glucose, 180.16; O_2, 31.9988; CO_2, 44.010; and H_2O, 18.015.

$$\text{mass of reactants} = \text{mass of products}$$

$$g\,glucose + g\,O_2 = g\,CO_2 + g\,H_2O$$

$$1\,mol\,glucose\left(\frac{180.16\,g}{1\,mol\,glucose}\right) + 6\,mol\,O_2\left(\frac{31.9988\,g}{1\,mol\,O_2}\right)$$

$$= 6\,mol\,CO_2\left(\frac{44.010\,g}{1\,mol\,CO_2}\right) + 6\,mol\,H_2O\left(\frac{18.015\,g}{1\,mol\,H_2O}\right)$$

$$372.15\,g = 372.15\,g$$

C One mole of glucose contains Avogadro's number (6.022×10^{23}) of glucose molecules. Thus 6.022×10^{23} glucose molecules react with ($6 \times 6.022 \times 10^{23}$) = 3.613×10^{24} oxygen molecules to yield ($6 \times 6.022 \times 10^{23}$) = 3.613×10^{24} molecules each of CO_2 and H_2O.

In tabular form:

Solution to Example 3.1.2

	$C_6H_{12}O_{6\ (s)}$	+	$6O_{2\ (g)}$	→	$6CO_{2\ (g)}$		$6H_2O_{(l)}$
a.	1 molecule		6 molecules		6 molecules		6 molecules
b.	1 mol		6 mol		6 mol		6 mol
c.	180.16 g		191.9928 g		264.06 g		108.09 g
d.	6.022×10^{23} molecules		3.613×10^{24} molecules		3.613×10^{24} molecules		3.613×10^{24} molecule

Exercise 3.1.2: Ammonium Nitrate Explosion

Ammonium nitrate is a common fertilizer, but under the wrong conditions it can be hazardous. In 1947, a ship loaded with ammonium nitrate caught fire during unloading and exploded, destroying the town of Texas City, Texas.



Ammonium nitrate can be hazardous. This aerial photograph of Texas City, Texas, shows the devastation caused by the explosion of a shipload of ammonium nitrate on April 16, 1947. For a video click here.

The explosion resulted from the following reaction:

$$2NH_4NO_{3\ (s)} \rightarrow 2N_{2\ (g)} + 4H_2O_{(g)} + O_{2\ (g)}$$

Construct a table showing how to interpret the information in the equation in terms of

a. individual molecules and ions.
b. moles of reactants and products.
c. grams of reactants and products given 2 mol of ammonium nitrate.
d. numbers of molecules or formula units of reactants and products given 2 mol of ammonium nitrate.

Answer:

Answer to Exercise 3.1.2

	$2NH_4NO_{3\ (s)}$	→	$2N_{2\ (g)}$	+	$4H_2O_{(g)}$	+	$O_{2\ (g)}$
a.	$2NH_4^+$ ions and $2NO_3^-$ ions		2 molecules		4 molecules		1 molecule

	$2NH_4NO_{3\ (s)}$	→	$2N_{2\ (g)}$	+	$4H_2O_{(g)}$	+	$O_{2\ (g)}$
b.	2 mol		2 mol		4 mol		1 mol
c.	160.0864 g		56.0268 g		72.0608 g		31.9988 g
d.	1.204×10^{24} formula units		1.204×10^{24} molecules		2.409×10^{24} molecules		6.022×10^{23} molecules

YouTube Video

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Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors (Mol Ratios): Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors, YouTube(opens in new window) [youtu.be]

Summary

A chemical reaction is described by a chemical equation that gives the identities and quantities of the reactants and the products. In a chemical reaction, one or more substances are transformed to new substances. A chemical reaction is described by a **chemical equation**, an expression that gives the identities and quantities of the substances involved in a reaction. A chemical equation shows the starting compound(s)—the **reactants**—on the left and the final compound(s)—the **products**—on the right, separated by an arrow. In a balanced chemical equation, the numbers of atoms of each element and the total charge are the same on both sides of the equation. The number of atoms, molecules, or formula units of a reactant or product in a balanced chemical equation is the **coefficient** of that species. The **mole ratio** of two substances in a chemical reaction is the ratio of their coefficients in the balanced chemical equation.

Answers

Exercise 3.1.1**: Fermentation**

$$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

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3.2: Some Simple Patterns of Chemical Reactivity

Learning Objectives

- To introduce the basic patterns of chemical reaction.

There is an underlying explanation of why a reaction takes place from an underlying chemical theory based on chemical reactivity. In this sections, we discussed various reactions to identify key chemical trends that allows chemists to predict the outcome of chemical reactions. By recognizing general patterns of chemical reactivity, you will be able to successfully predict the products formed by a given combination of reactants We can often predict a reaction if we have seen a similar reaction before. For example, sodium (Na) reacts with water ($\mathrm{H_2O}$) to form sodium hydroxide (NaOH) and $\mathrm{H_2}$ gas:

$$2\,\mathrm{Na\,(s)} + 2\,\mathrm{H_2O\,(l)} \longrightarrow 2\,\mathrm{NaOH\,(aq)} + \mathrm{H_2\,(g)}$$

with $\mathrm{(aq)}$ indicating aqueous liquid. As discussed later, potassium (K) is in the same family (column) of elements as sodium and exhibits similar chemistry. Therefore, one might *predict* that the reaction of K with $\mathrm{H_2O}$ would be similar to that of Na:

$$2\,\mathrm{K\,(s)} + 2\,\mathrm{H_2O\,(l)} \longrightarrow 2\,\mathrm{KOH\,(aq)} + \mathrm{H_2\,(g)}$$

In fact, all alkali metals react with water to form their hydroxide compounds and hydrogen.

Combination and Decomposition Reactions

In ***combination reactions,*** two or more compounds react to form a single, more complex compound. Many elements react with one another in this fashion to form compounds. The general chemical equation for combination reaction is:

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C}$$

and an example includes the generation of ammonia ($\mathrm{NH_3}$) from nitrogen ($\mathrm{N_2}$), and hydrogen ($\mathrm{H_2}$):

$$\mathrm{N_2\,(g)} + 3\,\mathrm{H_2\,(g)} \longrightarrow 2\,\mathrm{NH_3\,(g)}$$

In ***decomposition reactions*** one substance undergoes a reaction to form two or more simpler products. Such reactions often occur when compounds are heated or electricity is added. The general chemical equation for decomposition reaction is:

$$\mathrm{A} \longrightarrow \mathrm{B} + \mathrm{C}$$

For example, the thermal decomposition of limestone ($\mathrm{CaCO_3\,(s)}$) generates quicklime ($\mathrm{CaO\,(s)}$) and carbon dioxide $\mathrm{CO_2\,(g)}$

$$\mathrm{CaCO_3\,(s)} \longrightarrow \mathrm{CaO\,(s)} + \mathrm{CO_2\,(g)}$$

Combustion in Air

Combustion reactions are rapid reactions that produce a flame. Most common combustion reactions involve oxygen (O_2) from the air as a *reactant*. For example, wood will combust in the presence of oxygen in that air (with an ignition event) to generate a fire.



Figure 3.2.1: The flames caused as a result of a fuel undergoing combustion (burning) (CC BY-SA 2.5; Et bål via Wikipedia)

A common class of compounds which can participate in combustion reactions are *hydrocarbons* (compounds that contain only carbon and hydrogen).

Table 3.2.1: Examples of common hydrocarbons

Hydrocarbon	Molecular formula
methane	CH_4
propane	C_3H_8
butane	C_4H_{10}
octane	C_8H_{18}

When hydrocarbons are combusted they react with oxygen (O_2) to form carbon dioxide (CO_2) and water (H_2O). For example, when propane is burned the reaction is:

$$\mathrm{C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)} \tag{3.2.1}$$

Other compounds which contain carbon, hydrogen and oxygen (e.g. the alcohol *methanol* CH_3OH, and the sugar *glucose* $C_6H_{12}O_6$) also combust in the presence of oxygen (O_2) to produce CO_2 and H_2O.

Contributors and Attributions

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3.3: Formula Masses

Learning Objectives

- To determine the empirical formula of a compound from its composition by mass.
- To derive the molecular formula of a compound from its empirical formula.

When a new chemical compound, such as a potential new pharmaceutical, is synthesized in the laboratory or isolated from a natural source, chemists determine its elemental composition, its empirical formula, and its structure to understand its properties. This section focuses on how to determine the empirical formula of a compound and then use it to determine the molecular formula if the molar mass of the compound is known.

Formula and Molecular Weights

*The **formula weight** of a substance is the sum of the atomic weights of each atom in its chemical formula*. For example, water (H_2O) has a formula weight of:

$$2 \times (1.0079\ amu) + 1 \times (15.9994\ amu) = 18.01528\ amu$$

If a substance exists as discrete molecules (as with atoms that are *chemically bonded* together) then the *chemical formula* **is** the *molecular formula*, and the *formula weight* **is** the *molecular weight*. For example, carbon, hydrogen and oxygen can chemically bond to form a molecule of the sugar **glucose** with the chemical and molecular formula of $C_6H_{12}O_6$. The formula weight and the molecular weight of glucose is thus:

$$6 \times (12\ amu) + 12 \times (1.00794\ amu) + 6 \times (15.9994\ amu) = 180.0\ amu$$

Ionic substances are not chemically bonded and do not exist as discrete molecules. However, they do associate in discrete ratios of ions. Thus, we can describe their formula weights, but not their *molecular weights*. Table salt (NaCl), for example, has a formula weight of:

$$23.0\ amu + 35.5\ amu = 58.5\ amu$$

YouTube Video

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Molar Masses of Compounds, YouTube: Molar Masses of Compounds(opens in new window) [youtu.be]

Percentage Composition from Formulas

In some types of analyses of it is important to know the ***percentage by mass*** of each type of element in a compound. The law of definite proportions states that a chemical compound always contains the same proportion of elements by mass; that is, the percent composition—the percentage of each element present in a pure substance—is **constant** (although there are exceptions to this law). Take for example methane (CH_4) with a Formula and molecular weight:

$$1 \times (12.011\ amu) + 4 \times (1.008) = 16.043\ amu$$

the relative (mass) percentages of carbon and hydrogen are

$$\%C = \frac{1 \times (12.011\ amu)}{16.043 amu} = 0.749 = 74.9\%$$

$$\%H = \frac{4 \times (1.008\ amu)}{16.043\ amu} = 0.251 = 25.1\%$$

A more complex example is sucrose (table sugar), which is 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass. This means that 100.00 g of sucrose always contains 42.11 g of carbon, 6.48 g of hydrogen, and 51.41 g of oxygen. First the molecular formula of sucrose ($C_{12}H_{22}O_{11}$) is used to calculate the mass percentage of the component elements; the mass percentage can then be used to determine an **empirical formula**.

According to its molecular formula, each molecule of sucrose contains 12 carbon atoms, 22 hydrogen atoms, and 11 oxygen atoms. A mole of sucrose molecules therefore contains 12 mol of carbon atoms, 22 mol of hydrogen atoms, and 11 mol of oxygen atoms. This information can be used to calculate the mass of each element in 1 mol of sucrose, which gives the molar mass of sucrose. These masses can then be used to calculate the percent composition of sucrose. To three decimal places, the calculations are the following:

$$\text{mass of C/mol of sucrose} = 12\,mol\,C \times \frac{12.011\,g\,C}{1\,mol\,C} = 144.132\,g\,C \tag{3.3.1}$$

$$\text{mass of H/mol of sucrose} = 22\,mol\,H \times \frac{1.008\,g\,H}{1\,mol\,H} = 22.176\,g\,H \tag{3.3.2}$$

$$\text{mass of O/mol of sucrose} = 11\,mol\,O \times \frac{15.999\,g\,O}{1\,mol\,O} = 175.989\,g\,O \tag{3.3.3}$$

Thus 1 mol of sucrose has a mass of 342.297 g; note that more than half of the mass (175.989 g) is oxygen, and almost half of the mass (144.132 g) is carbon.

The mass percentage of each element in sucrose is the mass of the element present in 1 mol of sucrose divided by the molar mass of sucrose, multiplied by 100 to give a percentage. The result is shown to two decimal places:

$$\text{mass} = \frac{\text{mass of C/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{144.132\,g\,C}{342.297\,g/mol} \times 100 = 42.11\%$$

$$\text{mass} = \frac{\text{mass of H/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{22.176\,g\,H}{342.297\,g/mol} \times 100 = 6.48\%$$

$$\text{mass} = \frac{\text{mass of O/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{175.989\,g\,O}{342.297\,g/mol} \times 100 = 51.41\%$$

This can be checked by verifying that the sum of the percentages of all the elements in the compound is 100%:

$$42.11\% + 6.48\% + 51.41\% = 100.00\%$$

If the sum is not 100%, an error has been made in calculations. (Rounding to the correct number of decimal places can, however, cause the total to be slightly different from 100%.) Thus 100.00 g of sucrose contains 42.11 g of carbon, 6.48 g of hydrogen, and 51.41 g of oxygen; to two decimal places, the percent composition of sucrose is indeed 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen.

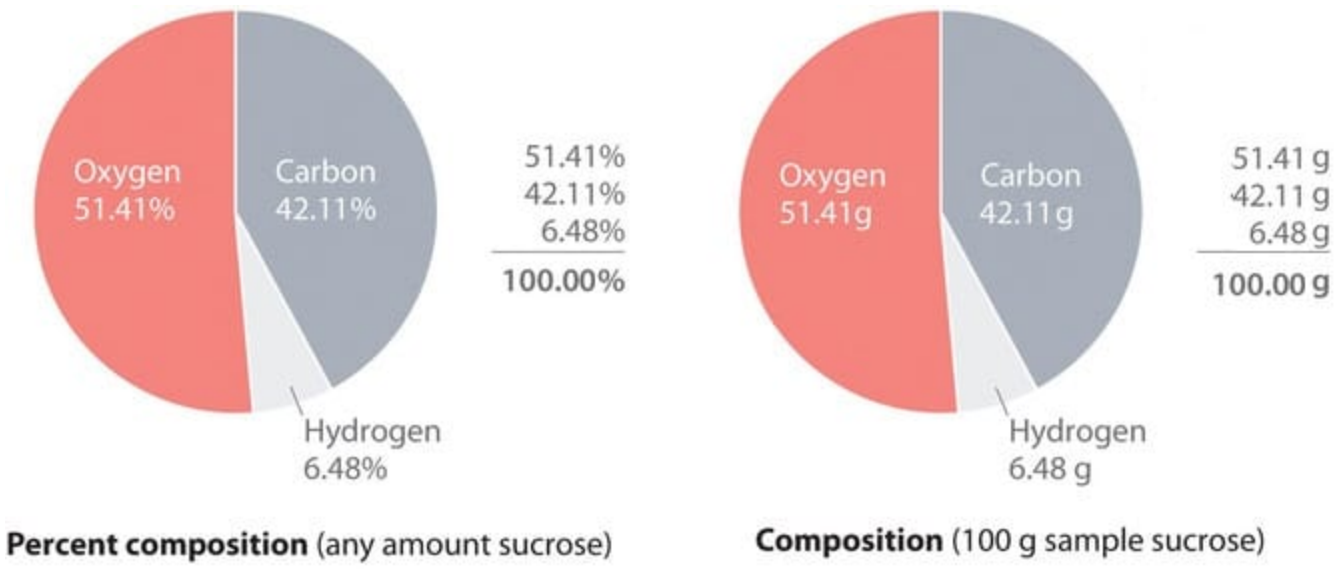
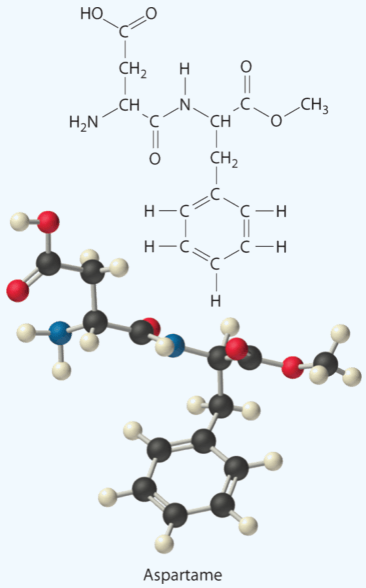


Figure 3.3.1: Percent and absolute composition of sucrose

It is also possible to calculate mass percentages using atomic masses and molecular masses, with atomic mass units. Because the answer is a ratio, expressed as a percentage, the units of mass cancel whether they are grams (using molar masses) or atomic mass units (using atomic and molecular masses).

Example 3.3.1: NutraSweet

Aspartame is the artificial sweetener sold as NutraSweet and Equal. Its molecular formula is $C_{14}H_{18}N_2O_5$.



Molecular Structure of Aspartame. (CC BY-NC-SA 3.0; anonymous)

a. Calculate the mass percentage of each element in aspartame.
b. Calculate the mass of carbon in a 1.00 g packet of Equal, assuming it is pure aspartame.

Given: molecular formula and mass of sample

Asked for: mass percentage of all elements and mass of one element in sample

Strategy:

A. Use atomic masses from the periodic table to calculate the molar mass of aspartame.
B. Divide the mass of each element by the molar mass of aspartame; then multiply by 100 to obtain percentages.
C. To find the mass of an element contained in a given mass of aspartame, multiply the mass of aspartame by the mass percentage of that element, expressed as a decimal.

Solution:

a.

A We calculate the mass of each element in 1 mol of aspartame and the molar mass of aspartame, here to three decimal places:

$$14\,C(14\,mol\,C)(12.011\,g/mol\,C) = 168.154\,g$$

$$18\,H(18\,mol\,H)(1.008\,g/mol\,H) = 18.144\,g$$

$$2\,N(2\,mol\,N)(14.007\,g/mol\,N) = 28.014\,g$$

$$+5\,O(5\,mol\,O)(15.999\,g/mol\,O) = 79.995\,g$$

$$C_{14}H_{18}N_2O_5 \text{molar mass of aspartame} = 294.307\,g/mol$$

Thus more than half the mass of 1 mol of aspartame (294.307 g) is carbon (168.154 g).

B To calculate the mass percentage of each element, we divide the mass of each element in the compound by the molar mass of aspartame and then multiply by 100 to obtain percentages, here reported to two decimal places:

$$mass\%\,C = \frac{168.154\,g\,C}{294.307\,g\,aspartame} \times 100 = 57.14\%C$$

$$mass\%\,H = \frac{18.144\,g\,H}{294.307\,g\,aspartame} \times 100 = 6.16\%H$$

$$mass\%\,N = \frac{28.014\,g\,N}{294.307\,g\,aspartame} \times 100 = 9.52\%$$

$$mass\%\,O = \frac{79.995\,g\,O}{294.307\,g\,aspartame} \times 100 = 27.18\%$$

As a check, we can add the percentages together:

$$57.14\% + 6.16\% + 9.52\% + 27.18\% = 100.00\%$$

If you obtain a total that differs from 100% by more than about ±1%, there must be an error somewhere in the calculation.

b. **C** The mass of carbon in 1.00 g of aspartame is calculated as follows:

$$\text{mass of C} = 1.00\,g\,aspartame \times \frac{57.14\,g\,C}{100\,g\,aspartame} = 0.571\,g\,C$$

Exercise 3.3.1: Aluminum Oxide

Calculate the mass percentage of each element in aluminum oxide (Al_2O_3). Then calculate the mass of aluminum in a 3.62 g sample of pure aluminum oxide.

Answer available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Percent Composition: Percent Composition, YouTube(opens in new window) [youtu.be]HNS6lItns10 (opens in new window)

Determining the Empirical Formula of Penicillin

Just as the empirical formula of a substance can be used to determine its percent composition, the percent composition of a sample can be used to determine its empirical formula, which can then be used to determine its molecular formula. Such a procedure was actually used to determine the empirical and molecular formulas of the first antibiotic to be discovered: penicillin.

Antibiotics are chemical compounds that selectively kill microorganisms, many of which cause diseases. Although antibiotics are often taken for granted today, penicillin was discovered only about 80 years ago. The subsequent development of a wide array of other antibiotics for treating many common diseases has contributed greatly to the substantial increase in life expectancy over the past 50 years. The discovery of penicillin is a historical detective story in which the use of mass percentages to determine empirical formulas played a key role.

In 1928, Alexander Fleming, a young microbiologist at the University of London, was working with a common bacterium that causes boils and other infections such as blood poisoning. For laboratory study, bacteria are commonly grown on the surface of a nutrient-containing gel in small, flat culture dishes. One day Fleming noticed that one of his cultures was contaminated by a bluish-green mold similar to the mold found on spoiled bread or fruit. Such accidents are rather common, and most laboratory workers would have simply thrown the cultures away. Fleming noticed, however, that the bacteria were growing everywhere on the gel except near the contaminating mold (part (a) in Figure 3.3.2), and he hypothesized that the mold must be producing a substance that either killed the bacteria or prevented their growth. To test this hypothesis, he grew the mold in a liquid and then filtered the liquid and added it to various bacteria cultures. The liquid killed not only the bacteria Fleming had originally been studying but also a wide range of other disease-causing bacteria. Because the mold was a member of the Penicillium family (named for their pencil-shaped branches under the microscope) (part (b) in Figure 3.3.2), Fleming called the active ingredient in the broth penicillin.

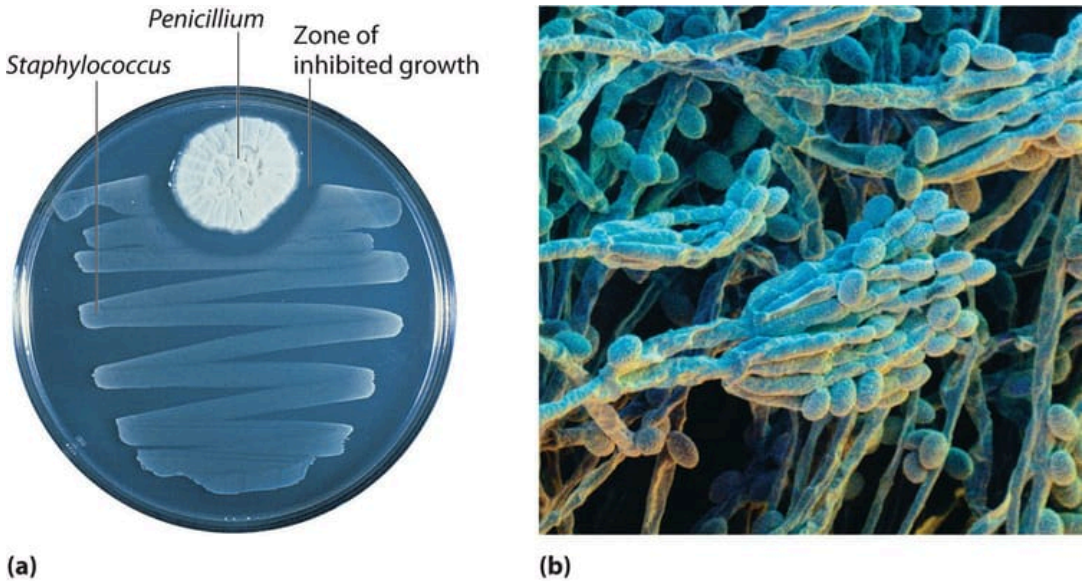


Figure 3.3.2: Penicillium. (a) Penicillium mold is growing in a culture dish; the photo shows its effect on bacterial growth. (b) In this photomicrograph of Penicillium, its rod- and pencil-shaped branches are visible. The name comes from the Latin penicillus, meaning "paintbrush."

A: Petri dish of Staphylococcus and penicillin. The ring around the penicillin where the Staphylococcus does not grow is labelled as the "zone of inhibition". B: Electron micrograph of Staphylococcus.

Although Fleming was unable to isolate penicillin in pure form, the medical importance of his discovery stimulated researchers in other laboratories. Finally, in 1940, two chemists at Oxford University, Howard Florey (1898–1968) and Ernst Chain (1906–1979), were able to isolate an active product, which they called penicillin G. Within three years, penicillin G was in widespread use for treating pneumonia, gangrene, gonorrhea, and other diseases, and its use greatly increased the survival rate of wounded soldiers in World War II. As a result of their work, Fleming, Florey, and Chain shared the Nobel Prize in Medicine in 1945.

As soon as they had succeeded in isolating pure penicillin G, Florey and Chain subjected the compound to a procedure called combustion analysis (described later in this section) to determine what elements were present and in what quantities. The results of such analyses are usually reported as mass percentages. They discovered that a typical sample of penicillin G contains 53.9% carbon, 4.8% hydrogen, 7.9% nitrogen, 9.0% sulfur, and 6.5% sodium by mass. The sum of these numbers is only 82.1%, rather than 100.0%, which implies that there must be one or more additional elements. A reasonable candidate is oxygen, which is a common component of compounds that contain carbon and hydrogen; do not assume that the "missing" mass is always due to oxygen. It could be any other element. For technical reasons, however, it is difficult to analyze for oxygen directly. Assuming that all the missing mass is due to oxygen, then penicillin G contains (100.0% – 82.1%) = 17.9% oxygen. From these mass percentages, the empirical formula and eventually the molecular formula of the compound can be determined.

To determine the empirical formula from the mass percentages of the elements in a compound such as penicillin G, the mass percentages must be converted to relative numbers of atoms. For convenience, assume a 100.0 g sample of the compound, even though the sizes of samples used for analyses are generally much smaller, usually in milligrams. This assumption simplifies the arithmetic because a 53.9% mass percentage of carbon corresponds to 53.9 g of carbon in a 100.0 g sample of penicillin G; likewise, 4.8% hydrogen corresponds to 4.8 g of hydrogen in 100.0 g of penicillin G; and so forth for the other elements. Each mass is then divided by the molar mass of the element to determine how many moles of each element are present in the 100.0 g sample:

$$\frac{mass\,(g)}{molar\ mass\ (g/mol)} = (g)\left(\frac{mol}{g}\right) = mol \tag{3.3.4}$$

$$53.9\,g\,C\left(\frac{1\,mol\,C}{12.011\,g\,C}\right) = 4.49\,mol\,C \tag{3.3.5}$$

$$4.8\,g\,H\left(\frac{1\,mol\,H}{1.008g\,H}\right) = 4.8\,mol\,H \tag{3.3.6}$$

$$7.9\,g\,N\left(\frac{1\,mol\,N}{14.007\,g\,N}\right) = 0.56\,mol\,N \tag{3.3.7}$$

$$9\,g\,S\left(\frac{1\,mol\,S}{32.065\,g\,S}\right)=0.28\,mol\,S \tag{3.3.8}$$

$$6.5\,g\,Na\left(\frac{1\,mol\,Na}{22.990\,g\,Na}\right)=0.28\,mol\,Na \tag{3.3.9}$$

Thus 100.0 g of penicillin G contains 4.49 mol of carbon, 4.8 mol of hydrogen, 0.56 mol of nitrogen, 0.28 mol of sulfur, 0.28 mol of sodium, and 1.12 mol of oxygen (assuming that all the missing mass was oxygen). The number of significant figures in the numbers of moles of elements varies between two and three because some of the analytical data were reported to only two significant figures.

These results give the ratios of the moles of the various elements in the sample (4.49 mol of carbon to 4.8 mol of hydrogen to 0.56 mol of nitrogen, and so forth), but they are not the whole-number ratios needed for the empirical formula—the empirical formula expresses the relative numbers of atoms in the smallest whole numbers possible. To obtain whole numbers, divide the numbers of moles of all the elements in the sample by the number of moles of the element present in the lowest relative amount, which in this example is sulfur or sodium. The results will be the subscripts of the elements in the empirical formula. To two significant figures, the results are as follows:

$$C:\frac{4.49}{0.28}=16\quad H:\frac{4.8}{0.28}=17\quad N:\frac{0.56}{0.28}=2.0 \tag{3.3.10}$$

$$S:\frac{0.28}{0.28}=1.0\quad Na:\frac{0.28}{0.28}=1.0\quad O:\frac{1.12}{0.28}=4.0 \tag{3.3.11}$$

The empirical formula of penicillin G is therefore $C_{16}H_{17}N_2NaO_4S$. Other experiments have shown that penicillin G is actually an ionic compound that contains Na^+ cations and $[C_{16}H_{17}N_2O_4S]^-$ anions in a 1:1 ratio. The complex structure of penicillin G (Figure 3.3.3) was not determined until 1948.

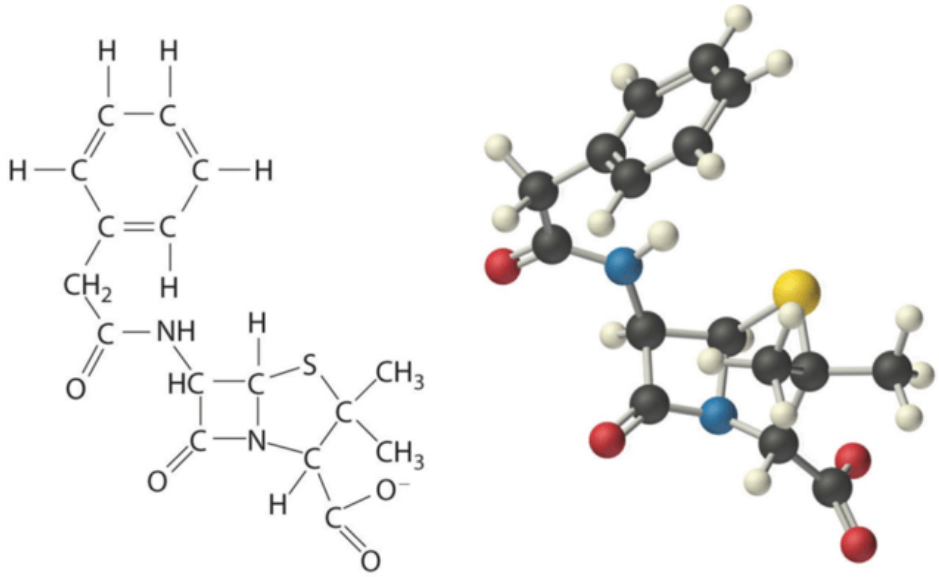


Figure 3.3.3: Structural Formula and Ball-and-Stick Model of the Anion of Penicillin G

In some cases, one or more of the subscripts in a formula calculated using this procedure may not be integers. Does this mean that the compound of interest contains a nonintegral number of atoms? No; rounding errors in the calculations as well as experimental errors in the data can result in nonintegral ratios. When this happens, judgment must be exercised in interpreting the results, as illustrated in Example 6. In particular, ratios of 1.50, 1.33, or 1.25 suggest that you should multiply all subscripts in the formula by 2, 3, or 4, respectively. Only if the ratio is within 5% of an integral value should one consider rounding to the

nearest integer.

Example 3.3.2: Calcium Phosphate in Toothpaste

Calculate the empirical formula of the ionic compound calcium phosphate, a major component of fertilizer and a polishing agent in toothpastes. Elemental analysis indicates that it contains 38.77% calcium, 19.97% phosphorus, and 41.27% oxygen.

Given: percent composition

Asked for: empirical formula

Strategy:

A. Assume a 100 g sample and calculate the number of moles of each element in that sample.
B. Obtain the relative numbers of atoms of each element in the compound by dividing the number of moles of each element in the 100 g sample by the number of moles of the element present in the smallest amount.
C. If the ratios are not integers, multiply all subscripts by the same number to give integral values.
D. Because this is an ionic compound, identify the anion and cation and write the formula so that the charges balance.

Solution:

A A 100 g sample of calcium phosphate contains 38.77 g of calcium, 19.97 g of phosphorus, and 41.27 g of oxygen. Dividing the mass of each element in the 100 g sample by its molar mass gives the number of moles of each element in the sample:

$$\text{moles Ca} = 38.77\,g\,Ca \times \frac{1\,mol\,Ca}{40.078\,g\,Ca} = 0.9674\,mol\,Ca$$

$$\text{moles P} = 19.97\,g\,P \times \frac{1\,mol\,P}{30.9738\,g\,P} = 0.6447\,mol\,Ca$$

$$\text{moles O} = 41.27\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 2.5800\,mol\,O$$

B To obtain the relative numbers of atoms of each element in the compound, divide the number of moles of each element in the 100-g sample by the number of moles of the element in the smallest amount, in this case phosphorus:

$$P: \frac{0.6447\,mol\,P}{0.6447\,mol\,P} = 1.000 \quad Ca: \frac{0.9674}{0.6447} = 1.501 \quad O: \frac{2.5800}{0.6447} = 4.002$$

C We could write the empirical formula of calcium phosphate as $Ca_{1.501}P_{1.000}O_{4.002}$, but the empirical formula should show the ratios of the elements as small whole numbers. To convert the result to integral form, multiply all the subscripts by 2 to get $Ca_{3.002}P_{2.000}O_{8.004}$. The deviation from integral atomic ratios is small and can be attributed to minor experimental errors; therefore, the empirical formula is $Ca_3P_2O_8$.

D The calcium ion (Ca^{2+}) is a cation, so to maintain electrical neutrality, phosphorus and oxygen must form a polyatomic anion. We know from Chapter 2 that phosphorus and oxygen form the phosphate ion (PO_4^{3-}; see Table 2.4). Because there are two phosphorus atoms in the empirical formula, two phosphate ions must be present. So we write the formula of calcium phosphate as $Ca_3(PO_4)_2$.

Exercise 3.3.2: Ammonium Nitrate

Calculate the empirical formula of ammonium nitrate, an ionic compound that contains 35.00% nitrogen, 5.04% hydrogen, and 59.96% oxygen by mass. Although ammonium nitrate is widely used as a fertilizer, it can be dangerously explosive. For example, it was a major component of the explosive used in the 1995 Oklahoma City bombing.



The Alfred P. Murrah Federal Building destroyed in the Oklahoma City bombing via chemical explosives (rapid chemical reactions that generate massive quantities of gases).

Answer available at the end of this section.

YouTube Video

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View this YouTube Video online

Determining Empirical and Molecular Formulas from % Composition: Determining Empirical and Molecular Formulas from % Composition, YouTube(opens in new window) [youtu.be]

From Empirical Formula to Molecular Formula

The empirical formula gives only the relative numbers of atoms in a substance in the smallest possible ratio. For a covalent substance, chemists are usually more interested in the molecular formula, which gives the actual number of atoms of each kind present per molecule. Without additional information, however, it is impossible to know whether the formula of penicillin G, for example, is $C_{16}H_{17}N_2NaO_4S$ or an integral multiple, such as $C_{32}H_{34}N_4Na_2O_8S_2$, $C_{48}H_{51}N_6Na_3O_{12}S_3$, or $(C_{16}H_{17}N_2NaO_4S)_n$, where n is an integer. (The actual structure of penicillin G is shown in Figure 3.3.3).

Consider glucose, the sugar that circulates in our blood to provide fuel for the body and brain. Results from combustion analysis of glucose report that glucose contains 39.68% carbon and 6.58% hydrogen. Because combustion occurs in the presence of oxygen, it is impossible to directly determine the percentage of oxygen in a compound by using combustion analysis; other more complex methods are necessary. Assuming that the remaining percentage is due to oxygen, then glucose would contain 53.79% oxygen. A 100.0 g sample of glucose would therefore contain 39.68 g of carbon, 6.58 g of hydrogen, and 53.79 g of oxygen. To calculate the number of moles of each element in the 100.0 g sample, divide the mass of each element by its molar mass:

$$moles\,C = 39.68\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 3.304\,mol\,C \tag{3.3.12}$$

$$moles\,H = 6.58\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 6.53\,mol\,H \tag{3.3.13}$$

$$moles\,O = 53.79\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 3.362\,mol\,O \tag{3.3.14}$$

Once again, the subscripts of the elements in the empirical formula are found by dividing the number of moles of each element by the number of moles of the element present in the smallest amount:

$$C: \frac{3.304}{3.304} = 1.000 \quad H: \frac{6.53}{3.304} = 1.98 \quad O: \frac{3.362}{3.304} = 1.018$$

The oxygen:carbon ratio is 1.018, or approximately 1, and the hydrogen:carbon ratio is approximately 2. The empirical formula of glucose is therefore CH_2O, but what is its molecular formula?

Many known compounds have the empirical formula CH_2O, including formaldehyde, which is used to preserve biological specimens and has properties that are very different from the sugar circulating in the blood. At this point, it cannot be known whether glucose is CH_2O, $C_2H_4O_2$, or any other $(CH_2O)_n$. However, the experimentally determined molar mass of glucose (180 g/mol) can be used to resolve this dilemma.

First, calculate the formula mass, the molar mass of the formula unit, which is the sum of the atomic masses of the elements in the empirical formula multiplied by their respective subscripts. For glucose,

$$\text{formula mass of} CH_2O = \left[1\,mol C\left(\frac{12.011\,g}{1\,mol\,C}\right)\right] + \left[2\,mol\,H\left(\frac{1.0079\,g}{1\,mol\,H}\right)\right] + \left[1\,mole\,O\left(\frac{15.5994\,mol\,O}{1\,mol\,O}\right)\right] = 30.026g \tag{3.3.15}$$

This is much smaller than the observed molar mass of 180 g/mol.

Second, determine the number of formula units per mole. For glucose, calculate the number of (CH_2O) units—that is, the n in $(CH_2O)_n$—by dividing the molar mass of glucose by the formula mass of CH_2O:

$$n = \frac{180\,g}{30.026\,g/CH_2O} = 5.99 \approx 6 CH_2O\,\text{formula units} \tag{3.3.16}$$

Each glucose contains six CH_2O formula units, which gives a molecular formula for glucose of $(CH_2O)_6$, which is more commonly written as $C_6H_{12}O_6$. The molecular structures of formaldehyde and glucose, both of which have the empirical formula CH_2O, are shown in Figure 3.3.4.

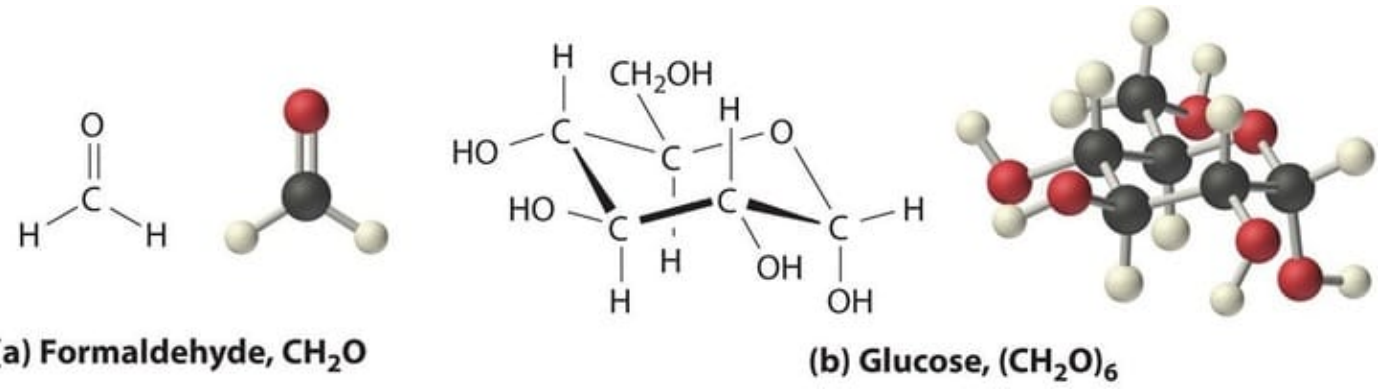


Figure 3.3.4: Structural Formulas and Ball-and-Stick Models of (a) Formaldehyde and (b) Glucose

Example 3.3.3: Caffeine

Calculate the molecular formula of caffeine, a compound found in coffee, tea, and cola drinks that has a marked stimulatory effect on mammals. The chemical analysis of caffeine shows that it contains 49.18% carbon, 5.39% hydrogen, 28.65% nitrogen, and 16.68% oxygen by mass, and its experimentally determined molar mass is 196 g/mol.

Given: percent composition and molar mass

Asked for: molecular formula

Strategy:

A. Assume 100 g of caffeine. From the percentages given, use the procedure given in Example 6 to calculate the empirical formula of caffeine.
B. Calculate the formula mass and then divide the experimentally determined molar mass by the formula mass. This gives the number of formula units present.
C. Multiply each subscript in the empirical formula by the number of formula units to give the molecular formula.

Solution:

A We begin by dividing the mass of each element in 100.0 g of caffeine (49.18 g of carbon, 5.39 g of hydrogen, 28.65 g of nitrogen, 16.68 g of oxygen) by its molar mass. This gives the number of moles of each element in 100 g of caffeine.

$$moles\,C = 49.18\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 4.095\,mol\,C$$

$$moles\,H = 5.39\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 5.35\,mol\,H$$

$$moles\,N = 28.65\,g\,N \times \frac{1\,mol\,N}{14.0067\,g\,N} = 2.045\,mol\,N$$

$$moles\,O = 16.68\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 1.043\,mol\,O$$

To obtain the relative numbers of atoms of each element present, divide the number of moles of each element by the number of moles of the element present in the least amount:

$$O: \frac{1.043}{1.043} = 1.000 \quad C: \frac{4.095}{1.043} = 3.926 \quad H: \frac{5.35}{1.043} = 5.13 \quad N: \frac{2.045}{1.043} = 1.960$$

These results are fairly typical of actual experimental data. None of the atomic ratios is exactly integral but all are within 5% of integral values. Just as in Example 6, it is reasonable to assume that such small deviations from integral values are due to minor experimental errors, so round to the nearest integer. The empirical formula of caffeine is thus $C_4H_5N_2O$.

B The molecular formula of caffeine could be $C_4H_5N_2O$, but it could also be any integral multiple of this. To determine the actual molecular formula, we must divide the experimentally determined molar mass by the formula mass. The formula mass is calculated as follows:

$$4C \quad (4\,atoms\,C)(12.011\,g/atom\,C) = 48.044\,g$$

$$5H \quad (5\,atoms\,H)(1.0079\,g/atom\,H) = 5.0395\,g$$

$$2N \quad (2\,atoms\,N)(14.0067\,g/atom\,N) = 28.0134\,g$$

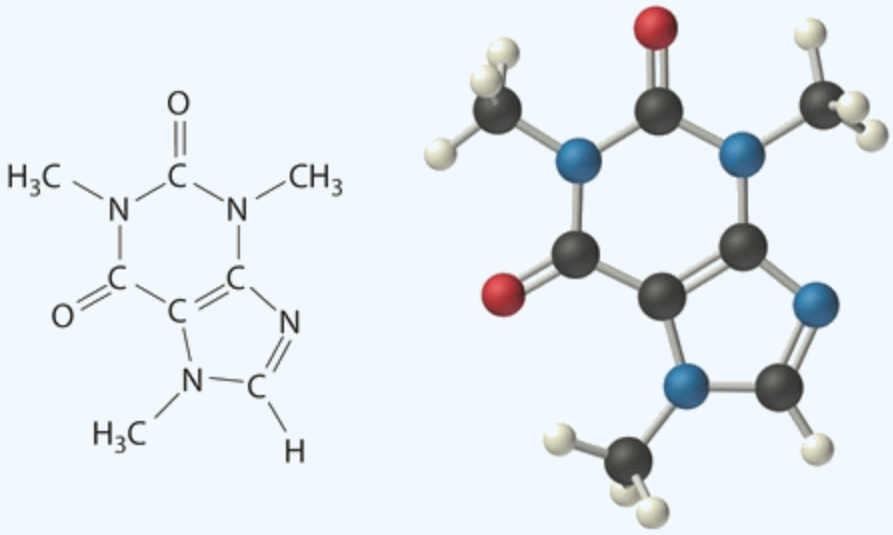
$$+1O \quad (1\,atom\,O)(15.9994\,g/atom\,O) = 15.9994\,g$$

$$C_4H_5N_2O \quad \text{formula mass of caffeine} = 97.096\,g$$

Dividing the measured molar mass of caffeine (196 g/mol) by the calculated formula mass gives

$$\frac{196 g/mol}{97.096 g/C_4H_5N_2O} = 2.02 \approx 2\,C_4H_5N_2O\,\text{empirical formula units}$$

C There are two $C_4H_5N_2O$ formula units in caffeine, so the molecular formula must be $(C_4H_5N_2O)_2 = C_8H_{10}N_4O_2$. The structure of caffeine is as follows:



Caffeine

Exercise 3.3.3: Freon-114

Calculate the molecular formula of Freon-114, which has 13.85% carbon, 41.89% chlorine, and 44.06% fluorine. The experimentally measured molar mass of this compound is 171 g/mol. Like Freon-11, Freon-114 is a commonly used refrigerant that has been implicated in the destruction of the ozone layer.



Answer available at the end of this section.

Summary

The empirical formula of a substance can be calculated from its percent composition, and the molecular formula can be determined from the empirical formula and the compound's molar mass. The empirical formula of a substance can be calculated from the experimentally determined percent composition, the percentage of each element present in a pure substance by mass. In many cases, these percentages can be determined by combustion analysis. If the molar mass of the compound is known, the molecular formula can be determined from the empirical formula.

Contributors and Attributions

- Mike Blaber (Florida State University)

Answers

Exercise 3.3.1: Aluminum Oxide

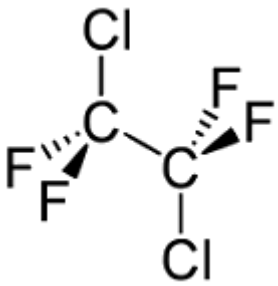
52.93% aluminum; 47.08% oxygen; 1.92 g Al

Exercise 3.3.2: Ammonium Nitrate

$N_2H_4O_3$ is $NH_4^+NO_3^-$, written as NH_4NO_3

Exercise 3.3.3: Freon-114

$C_2Cl_2F_4$



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3.4: Avogadro's Number and the Mole

Learning Objectives

- To calculate the molecular mass of a covalent compound and the formula mass of an ionic compound, and to calculate the number of atoms, molecules, or formula units in a sample of a substances.

As discussed previosuly, the **mass number** is the sum of the numbers of protons and neutrons present in the nucleus of an atom. The mass number is an integer that is approximately equal to the numerical value of the atomic mass. Although the mass number is unitless, it is assigned units called **atomic mass units (amu)**. Because a molecule or a polyatomic ion is an assembly of atoms whose identities are given in its molecular or ionic formula, the average atomic mass of any molecule or polyatomic ion can be calculated from its composition by adding together the masses of the constituent atoms. The average mass of a monatomic ion is the same as the average mass of an atom of the element because the mass of electrons is so small that it is insignificant in most calculations.

Molecular and Formula Masses

The molecular mass of a substance is the sum of the average masses of the atoms in one molecule of a substance. It is calculated by adding together the atomic masses of the elements in the substance, each multiplied by its subscript (written or implied) in the molecular formula. Because the units of atomic mass are atomic mass units, the units of molecular mass are also atomic mass units. The procedure for calculating molecular masses is illustrated in Example $3.4.1$.

Example $3.4.1$: Molecular Mass of Ethanol

Calculate the molecular mass of ethanol, whose condensed structural formula is $\mathrm{CH_3CH_2OH}$. Among its many uses, ethanol is a fuel for internal combustion engines.

Given: molecule

Asked for: molecular mass

Strategy:

A. Determine the number of atoms of each element in the molecule.
B. Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.
C. Add together the masses to give the molecular mass.

Solution:

A The molecular formula of ethanol may be written in three different ways: $\mathrm{CH_3CH_2OH}$ (which illustrates the presence of an ethyl group, CH_3CH_2–, and an –OH group), $\mathrm{C_2H_5OH}$, and $\mathrm{C_2H_6O}$; all show that ethanol has two carbon atoms, six hydrogen atoms, and one oxygen atom.

B Taking the atomic masses from the periodic table, we obtain

$$2 \times \text{ atomic mass of carbon} = 2\,atoms\left(\frac{12.011\,amu}{atoms}\right)$$
$$= 24.022\,amu$$

$$6 \times \text{ atomic mass of hydrogen} = 2\,atoms\left(\frac{1.0079\,amu}{atoms}\right)$$
$$= 6.0474\,amu$$

$$1 \times \text{ atomic mass of oxygen} = 1\,atoms\left(\frac{15.9994\,amu}{atoms}\right)$$
$$= 15.994\,amu$$

C Adding together the masses gives the molecular mass:

$$24.022\,amu + 6.0474\,amu + 15.9994\,amu = 46.069\,amu$$

Alternatively, we could have used unit conversions to reach the result in one step:

$$\left[2\,atoms\,C\left(\frac{12.011\,amu}{1\,atomC}\right)\right] + \left[6\,atoms\,H\left(\frac{1.0079\,amu}{1\,atomH}\right)\right] + \left[1\,atoms\,C\left(\frac{15.9994\,amu}{1\,atom0}\right)\right] = 46.069\,amu$$

The same calculation can also be done in a tabular format, which is especially helpful for more complex molecules:

$$2 \times C \;\; (2\,atoms)(12.011\,amu/atom) = 24.022\,amu$$

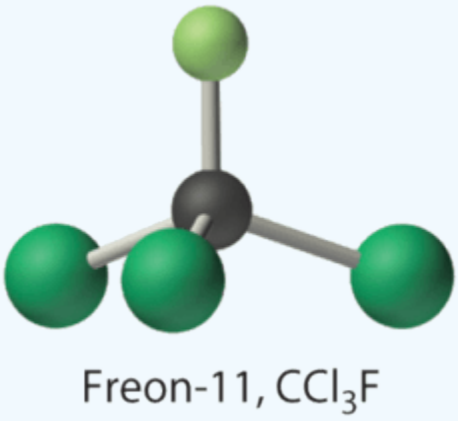
$$6 \times H \;\; (6\,atoms)(1.0079\,amu/atom) = 6.0474\,amu$$

$$1 \times O \;\; (1\,atoms)(15.9994\,amu/atom) = 15.9994\,amu$$

$$C_2H_6O \quad \text{molecular mass of ethanol} = 46.069\,amu$$

Exercise 3.4.1: Molecular Mass of Freon

Calculate the molecular mass of trichlorofluoromethane, also known as Freon-11, whose condensed structural formula is CCl_3F. Until recently, it was used as a refrigerant. The structure of a molecule of Freon-11 is as follows:



Answer available at the end of this section.

Unlike molecules, which form covalent bonds, ionic compounds do not have a readily identifiable molecular unit. Therefore, for ionic compounds, the formula mass (also called the empirical formula mass) of the compound is used instead of the molecular mass. The formula mass is the sum of the atomic masses of all the elements in the empirical formula, each multiplied by its subscript (written or implied). It is directly analogous to the molecular mass of a covalent compound. The units are atomic mass units.

Atomic mass, molecular mass, and formula mass all have the same units: atomic mass units.

Example 3.4.2: Formula Mass of Calcium Phosphate

Calculate the formula mass of $Ca_3(PO_4)_2$, commonly called calcium phosphate. This compound is the principal source of calcium found in bovine milk.

Given: ionic compound

Asked for: formula mass

Strategy:

A. Determine the number of atoms of each element in the empirical formula.
B. Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.
C. Add together the masses to give the formula mass.

Solution:

A The empirical formula—$Ca_3(PO_4)_2$—indicates that the simplest electrically neutral unit of calcium phosphate contains three Ca^{2+} ions and two PO_4^{3-} ions. The formula mass of this molecular unit is calculated by adding together the atomic masses of three calcium atoms, two phosphorus atoms, and eight oxygen atoms.

B Taking atomic masses from the periodic table, we obtain

$$3 \times \text{atomic mass of calcium} = 3\,atoms\left(\frac{40.078\,amu}{atom}\right) = 120.234\,amu$$

$$2 \times \text{atomic mass of phosphorus} = 2\,atoms\left(\frac{30.973761\,amu}{atom}\right) = 61.947522\,amu$$

$$8 \times \text{atomic mass of oxygen} = 8\,atoms\left(\frac{15.9994\,amu}{atom}\right) = 127.9952\,amu$$

C Adding together the masses gives the formula mass of $Ca_3(PO_4)_2$:

$$120.234\,amu + 61.947522\,amu + 127.9952\,amu = 310.177\,amu$$

We could also find the formula mass of $Ca_3(PO_4)_2$ in one step by using unit conversions or a tabular format:

$$\left[3\,atoms Ca\left(\frac{40.078\,amu}{1\,atom Ca}\right)\right] + \left[2\,atoms P\left(\frac{30.973761\,amu}{1\,atom P}\right)\right] + \left[8\,atoms O\left(\frac{15.9994\,amu}{1\,atom O}\right)\right] = 310.177\,amu$$

$$3Ca \quad (3\,atoms)(40.078\,amu/atom) = 120.234\,amu$$

$$2P \quad (2\,atoms)(30.973761\,amu/atom) = 61.947522\,amu$$

$$+8O \quad (8\,atoms)(15.9994\,amu/atom) = 127.9952\,amu$$

$$Ca_3P_2O_8 \quad \text{formula mass of } Ca_3(PO_4)_2 = 310.177\,amu$$

Exercise 3.4.2: Formula Mass of Silicon Nitride

Calculate the formula mass of Si_3N_4, commonly called silicon nitride. It is an extremely hard and inert material that is used to make cutting tools for machining hard metal alloys.

Answer available at the end of this section.

YouTube Video

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Molar Masses of Compounds: Molar Masses of Compounds, YouTube(opens in new window) [youtu.be]

The Mole

Dalton's theory that each chemical compound has a particular combination of atoms and that the ratios of the numbers of atoms of the elements present are usually small whole numbers. It also describes the law of multiple proportions, which states that the ratios of the masses of elements that form a series of compounds are small whole numbers. The problem for Dalton and other early chemists was to discover the quantitative relationship between the number of atoms in a chemical substance and its mass. Because the masses of individual atoms are so minuscule (on the order of 10^{-23} g/atom), chemists do not measure the mass of individual atoms or molecules. In the laboratory, for example, the masses of compounds and elements used by chemists typically range from milligrams to grams, while in industry, chemicals are bought and sold in kilograms and tons. To analyze the transformations that occur between individual atoms or molecules in a chemical reaction, it is therefore essential for chemists to know how many atoms or molecules are contained in a measurable quantity in the laboratory—a given mass of sample. The unit that provides this link is the mole (mol), from the Latin *mole*s, meaning "pile" or "heap."

Many familiar items are sold in numerical quantities with distinct names. For example, cans of soda come in a six-pack, eggs are sold by the dozen (12), and pencils often come in a gross (12 dozen, or 144). Sheets of printer paper are packaged in reams of 500, a seemingly large number. Atoms are so small, however, that even 500 atoms are too small to see or measure by most common techniques. Any readily measurable mass of an element or compound contains an extraordinarily large number of atoms, molecules, or ions, so an extremely large numerical unit is needed to count them. The mole is used for this purpose.

A mole is defined as the amount of a substance that contains the number of carbon atoms in exactly 12 g of isotopically pure carbon-12. According to the most recent experimental measurements, this mass of carbon-12 contains 6.022142×10^{23} atoms, but for most purposes 6.022×10^{23} provides an adequate number of significant figures. Just as 1 mole of atoms contains 6.022×10^{23} atoms, 1 mole of eggs contains 6.022×10^{23} eggs. This number is called Avogadro's number, after the 19th-century Italian scientist who first proposed a relationship between the volumes of gases and the numbers of particles they contain.

It is not obvious why eggs come in dozens rather than 10s or 14s, or why a ream of paper contains 500 sheets rather than 400 or 600. The definition of a mole—that is, the decision to base it on 12 g of carbon-12—is also arbitrary. The important point is that 1 mole of carbon—or of anything else, whether atoms, compact discs, or houses—always has the same number of objects: 6.022×10^{23}.

> One mole always has the same number of objects: 6.022 × 1023.

To appreciate the magnitude of Avogadro's number, consider a mole of pennies. Stacked vertically, a mole of pennies would be 4.5×10^{17} mi high, or almost six times the diameter of the Milky Way galaxy. If a mole of pennies were distributed equally among the entire population on Earth, each person would have more than one trillion dollars. The mole is so large that it is useful only for measuring very small objects, such as atoms.

The concept of the mole allows scientists to count a specific number of individual atoms and molecules by weighing measurable quantities of elements and compounds. To obtain 1 mol of carbon-12 atoms, one weighs out 12 g of isotopically pure carbon-12. Because each element has a different atomic mass, however, a mole of each element has a different mass, even though it contains the same number of atoms (6.022×10^{23}). This is analogous to the fact that a dozen extra large eggs weighs more than a dozen small eggs, or that the total weight of 50 adult humans is greater than the total weight of 50 children. Because of the way the mole is defined, for every element the number of grams in a mole is the same as the number of atomic mass units in the atomic

mass of the element. For example, the mass of 1 mol of magnesium (atomic mass = 24.305 amu) is 24.305 g. Because the atomic mass of magnesium (24.305 amu) is slightly more than twice that of a carbon-12 atom (12 amu), the mass of 1 mol of magnesium atoms (24.305 g) is slightly more than twice that of 1 mol of carbon-12 (12 g). Similarly, the mass of 1 mol of helium (atomic mass = 4.002602 amu) is 4.002602 g, which is about one-third that of 1 mol of carbon-12. Using the concept of the mole, Dalton's theory can be restated: 1 mol of a compound is formed by combining elements in amounts whose mole ratios are small whole numbers. For example, 1 mol of water (H_2O) has 2 mol of hydrogen atoms and 1 mol of oxygen atoms.

Molar Mass

The molar mass of a substance is defined as the mass in grams of 1 mole of that substance. One mole of isotopically pure carbon-12 has a mass of 12 g. For an element, the molar mass is the mass of 1 mol of atoms of that element; for a covalent molecular compound, it is the mass of 1 mol of molecules of that compound; for an ionic compound, it is the mass of 1 mol of formula units. That is, the molar mass of a substance is the mass (in grams per mole) of 6.022×10^{23} atoms, molecules, or formula units of that substance. In each case, the number of grams in 1 mol is the same as the number of atomic mass units that describe the atomic mass, the molecular mass, or the formula mass, respectively.

> The molar mass of any substance is its atomic mass, molecular mass, or formula mass in grams per mole.

The periodic table lists the atomic mass of carbon as 12.011 amu; the average molar mass of carbon—the mass of 6.022×10^{23} carbon atoms—is therefore 12.011 g/mol:

Atomic mass of carbon as 12.011 amu; the average molar mass of carbon

Substance (formula)	Atomic, Molecular, or Formula Mass (amu)	Molar Mass (g/mol)
carbon (C)	12.011 (atomic mass)	12.011
ethanol (C_2H_5OH)	46.069 (molecular mass)	46.069
calcium phosphate [$Ca_3(PO_4)_2$]	310.177 (formula mass)	310.177

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Determining the Molar Mass of a Molecule, YouTube: Determining the Molar Mass of a Molecule(opens in new window) [youtu.be]

The molar mass of naturally-occurring carbon is different from that of carbon-12, and is not an integer because carbon occurs as a mixture of carbon-12, carbon-13, and carbon-14. One mole of carbon still has 6.022×10^{23} carbon atoms, but 98.89% of those atoms are carbon-12, 1.11% are carbon-13, and a trace (about 1 atom in 1012) are carbon-14. (For more information, see Section 1.6.) Similarly, the molar mass of uranium is 238.03 g/mol, and the molar mass of iodine is 126.90 g/mol. When dealing with elements such as iodine and sulfur, which occur as a diatomic molecule (I_2) and a polyatomic molecule (S_8), respectively, molar mass usually refers to the mass of 1 mol of atoms of the element—in this case I and S, not to the mass of 1 mol of molecules of the element (I_2 and S_8).

The molar mass of ethanol is the mass of ethanol (C_2H_5OH) that contains 6.022×10^{23} ethanol molecules. As in Example 3.4.1, the molecular mass of ethanol is 46.069 amu. Because 1 mol of ethanol contains 2 mol of carbon atoms (2 × 12.011 g), 6 mol of hydrogen atoms (6 × 1.0079 g), and 1 mol of oxygen atoms (1 × 15.9994 g), its molar mass is 46.069 g/mol. Similarly, the formula mass of calcium phosphate [$Ca_3(PO_4)_2$] is 310.177 amu, so its molar mass is 310.177 g/mol. This is the mass of calcium phosphate that contains 6.022×10^{23} formula units.

The mole is the basis of quantitative chemistry. It provides chemists with a way to convert easily between the mass of a substance and the number of individual atoms, molecules, or formula units of that substance. Conversely, it enables chemists to calculate the mass of a substance needed to obtain a desired number of atoms, molecules, or formula units. For example, to convert moles of a substance to mass, the following relationship is used:

$$(\text{moles}) \times (\text{molar mass}) \rightarrow \text{mass} \tag{3.4.1}$$

or, more specifically,

$$\cancel{\text{moles}} \times \left(\frac{\text{grams}}{\cancel{\text{mole}}}\right) = \text{grams}$$

Conversely, to convert the mass of a substance to moles:

$$\left(\frac{\text{grams}}{\text{molar mass}}\right) \rightarrow \text{moles} \tag{3.4.2}$$

$$\left(\frac{\text{grams}}{\text{grams/mole}}\right) = \cancel{\text{grams}}\left(\frac{\text{mole}}{\cancel{\text{grams}}}\right) = \text{moles} \tag{3.4.3}$$

The coefficients in a balanced chemical equation can be interpreted both as the relative numbers of molecules involved in the reaction and as the relative number of moles. For example, in the *balanced* equation:

$$2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \rightarrow 2\,\mathrm{H_2O}(\ell)$$

the production of two moles of water would require the consumption of 2 moles of $\mathrm{H_2}$ and one mole of $\mathrm{O_2}$. Therefore, when considering ***this*** particular reaction

- **2 moles** of $\mathrm{H_2}$
- **1 mole** of $\mathrm{O_2}$ and
- **2 moles** of $\mathrm{H_2O}$

would be considered to be ***stoichiometrically equivalent quantitites***.

These stoichiometric relationships, derived from balanced equations, can be used to determine expected amounts of products given amounts of reactants. For example, how many moles of H_2O would be produced from 1.57 moles of O_2?

$$(1.57\ mol\ \mathrm{O_2})\left(\frac{2\ mol\,\mathrm{H_2O}}{1\ mol\ \mathrm{O_2}}\right) = 3.14\ mol\ \mathrm{H_2O}$$

The ratio $\left(\frac{2\ mol\ \mathrm{H_2O}}{1\ mol\ \mathrm{O_2}}\right)$ is the stoichiometric relationship between $\mathrm{H_2O}$ and $\mathrm{O_2}$ from the balanced equation for this reaction.

Be sure to pay attention to the units when converting between mass and moles. Figure $3.4.1$ is a flowchart for converting between mass; the number of moles; and the number of atoms, molecules, or formula units. The use of these conversions is illustrated in Examples $3.4.3$ and $3.4.4$.

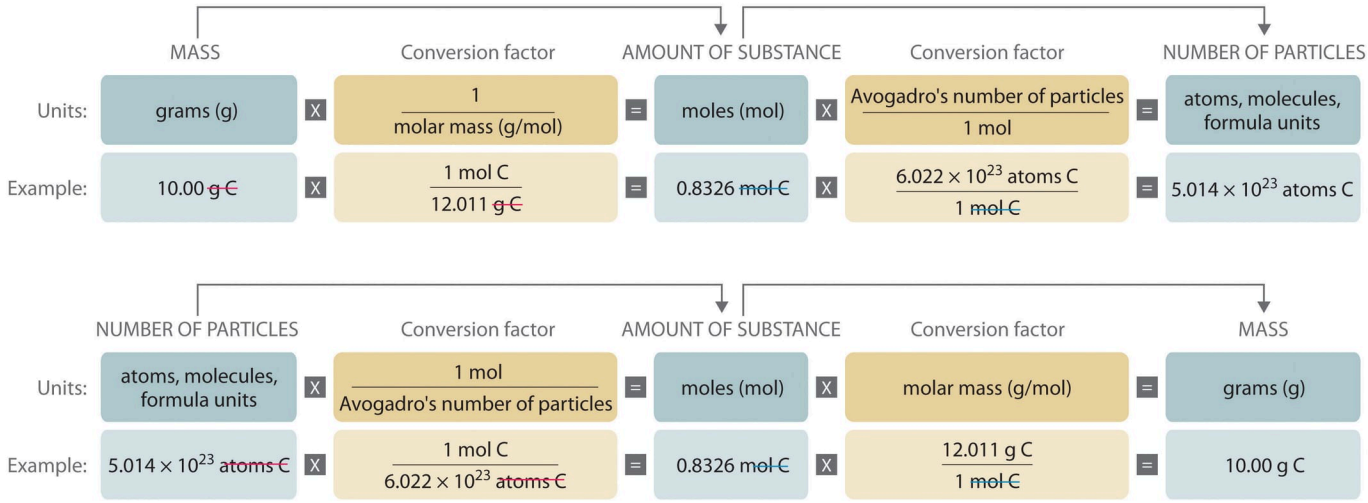


Figure 3.4.1: A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units
Flowchart of conversions between mass, amount of substance, and number of particles using conversion factors of molar mass and Avogadro's number.

Example 3.4.3: Combustion of Butane

For the combustion of butane (C_4H_{10}) the balanced equation is:

$$2\,C_4H_{10}\,(l) + 13\,O_2\,(g) \rightarrow 8\,CO_2\,(g) + 10\,H_2O\,(l)$$

Calculate the mass of CO_2 that is produced in burning 1.00 gram of C_4H_{10}.

Solution

Thus, the overall sequence of steps to solve this problem is:



First of all we need to calculate how many moles of butane we have in a 1.00 gram sample:

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ {}_4CH_{10}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right)$$

Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ {}_4CH_{10} = 6.88 \times 10^{-2}\ mol\ CO_2$$

The question called for the determination of the mass of CO_2 produced, thus we have to convert moles of CO_2 into grams (by using the **molecular weight** of CO_2):

$$6.88 \times 10^{-2}\ mol\ CO_2 \left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2} \right) = 3.03\ g\ CO_2$$

Example 3.4.4: Ethylene Glycol

For 35.00 g of ethylene glycol (\ce{HOCH2CH2OH}), which is used in inks for ballpoint pens, calculate the number of

a. moles.
b. molecules.

Given: mass and molecular formula

Asked for: number of moles and number of molecules

Strategy:

A. Use the molecular formula of the compound to calculate its molecular mass in grams per mole.
B. Convert from mass to moles by dividing the mass given by the compound's molar mass.
C. Convert from moles to molecules by multiplying the number of moles by Avogadro's number.

Solution:

A The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 3.4.1:

$$2C(2\,atoms)(12.011\,amu/atom) = 24.022\,amu$$

$$6H(6\,atoms)(1.0079\,amu/atom) = 6.0474\,amu$$

$$2O(2\,atoms)(15.9994\,amu/atom) = 31.9988\,amu$$

$$C_2H_6O_2 \text{molecular mass of ethylene glycol} = 62.068\,amu$$

The molar mass of ethylene glycol is 62.068 g/mol.

B The number of moles of ethylene glycol present in 35.00 g can be calculated by dividing the mass (in grams) by the molar mass (in grams per mole):

$$\frac{\text{mass of ethylene glycol (g)}}{\text{molar mass (g/mol)}} = \text{moles ethylene glycol (mol)}$$

So

$$35.00\,g \text{ethylene glycol} \left(\frac{1\,mole\,\text{ethylene glycol}}{62.068\,g\,\text{ethylene glycol}} \right) = 0.5639\,mol \text{ethylene glycol}$$

It is always a good idea to estimate the answer before you do the actual calculation. In this case, the mass given (35.00 g) is less than the molar mass, so the answer should be less than 1 mol. The calculated answer (0.5639 mol) is indeed less than 1 mol, so we have probably not made a major error in the calculations.

C To calculate the number of molecules in the sample, we multiply the number of moles by Avogadro's number:

$$\text{molecules of ethylene glycol} = 0.5639\ \cancel{mol} \left(\frac{6.022 \times 10^{23}\ molecules}{1\ \cancel{mol}} \right)$$

$$= 3.396 \times 10^{23}\ molecules$$

Because we are dealing with slightly more than 0.5 mol of ethylene glycol, we expect the number of molecules present to be slightly more than one-half of Avogadro's number, or slightly more than 3×10^{23} molecules, which is indeed the case.

Exercise 3.4.4: Freon-11

For 75.0 g of CCl_3F (Freon-11), calculate the number of

a. moles.
b. molecules.

Answer a available at the end of this section.

Example 3.4.5

Calculate the mass of 1.75 mol of each compound.

a. S_2Cl_2 (common name: sulfur monochloride; systematic name: disulfur dichloride)
b. $Ca(ClO)_2$ (calcium hypochlorite)

Given: number of moles and molecular or empirical formula

Asked for: mass

Strategy:

A Calculate the molecular mass of the compound in grams from its molecular formula (if covalent) or empirical formula (if ionic).

B Convert from moles to mass by multiplying the moles of the compound given by its molar mass.

Solution:

We begin by calculating the molecular mass of S_2Cl_2 and the formula mass of $Ca(ClO)_2$.

A The molar mass of S_2Cl_2 is obtained from its molecular mass as follows:

$$2S(2\,atoms)(32.065\,amu/atom) = 64.130\,amu$$

$$+2Cl(2\,atoms)(35.453\,amu/atom) = 70.906\,amu$$

$$S_2Cl_2 \text{molecular mass of } S_2Cl_2 = 135.036\,amu$$

The molar mass of S_2Cl_2 is 135.036 g/mol.

B The mass of 1.75 mol of S_2Cl_2 is calculated as follows:

$$moles S_2Cl_2 \left[\text{molar mass}\left(\frac{g}{mol}\right)\right] \rightarrow mass of S_2Cl_2\,(g)$$

$$1.75\,mol S_2Cl_2 \left(\frac{135.036\,g S_2Cl_2}{1\,mol S_2Cl_2}\right) = 236\,g S_2Cl_2$$

A The formula mass of $Ca(ClO)_2$ is obtained as follows:

$$1Ca(1\,atom)(40.078\,amu/atom) = 40.078\,amu$$

$$2Cl(2\,atoms)(35.453\,amu/atom) = 70.906\,amu$$

$$+2O(2\,atoms)(15.9994\,amu/atom) = 31.9988\,amu$$

$$Ca(ClO)_2 \text{ formula mass of } Ca(ClO)_2 = 142.983\,amu$$

The molar mass of $Ca(ClO)_2$ 142.983 g/mol.

B The mass of 1.75 mol of $Ca(ClO)_2$ is calculated as follows:

$$molesCa(ClO)_2\left[\frac{\text{molar mass}Ca(ClO)_2}{1\,molCa(ClO)_2}\right] = massCa(ClO)_2$$

$$1.75\,molCa(ClO)_2\left[\frac{142.983\,gCa(ClO)_2}{1\,molCa(ClO)_2}\right] = 250\,gCa(ClO)_2$$

Because 1.75 mol is less than 2 mol, the final quantity in grams in both cases should be less than twice the molar mass, which it is.

Exercise 3.4.5

Calculate the mass of 0.0122 mol of each compound.

a. Si_3N_4 (silicon nitride), used as bearings and rollers
b. $(CH_3)_3N$ (trimethylamine), a corrosion inhibitor

Answer a available at the end of this section.

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Conversions Between Grams, Mol, & Atoms: Conversions Between Grams, Mol & Atoms, YouTube(opens in new window) [youtu.be]

The coefficients in a balanced chemical equation can be interpreted both as the relative numbers of molecules involved in the reaction and as the relative number of moles. For example, in the *balanced* equation:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(l)$$

the production of two moles of water would require the consumption of 2 moles of H_2 and one mole of O_2. Therefore, when considering ***this*** particular reaction

- **2 moles** of H_2
- **1 mole** of O_2 and
- **2 moles** of H_2O

would be considered to be ***stoichiometrically equivalent quantitites***.

These stoichiometric relationships, derived from balanced equations, can be used to determine expected amounts of products given amounts of reactants. For example, how many moles of H_2O would be produced from 1.57 moles of O_2?

$$(1.57\ mol\ O_2)\left(\frac{2\ mol H_2O}{1\ mol\ O_2}\right) = 3.14\ mol\ H_2O$$

The ratio $\left(\frac{2\ mol \backslash 1 H_2O}{1\ mol\ O_2}\right)$ is the stoichiometric relationship between H_2O and O_2 from the balanced equation for this reaction.

Example 3.4.6

For the combustion of butane (C_4H_{10}) the balanced equation is:

$$2\,C_4H_{10}\,(l) + 13\,O_2\,(g) \rightarrow 8\,CO_2\,(g) + 10\,H_2O\,(l)$$

Calculate the mass of CO_2 that is produced in burning 1.00 gram of C_4H_{10}.

Solution

First of all we need to calculate how many moles of butane we have in a 1.00 gram sample:

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ C_4H_{10}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right)$$

Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ C_4H_{10} = 6.88 \times 10^{-2}\ mol\ CO_2$$

The question called for the determination of the mass of CO_2 produced, thus we have to convert moles of CO_2 into grams (by using the **molecular weight** of CO_2):

$$6.88 \times 10^{-2}\ mol\ CO_2\left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2}\right) = 3.03\ g\ CO_2$$

Thus, the overall sequence of steps to solve this problem were:



In a similar way we could determine the mass of water produced, or oxygen consumed, etc.

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Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors (Mol Ratios): Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors (Mol Ratios), YouTube(opens in new window) [youtu.be]

Summary

To analyze chemical transformations, it is essential to use a standardized unit of measure called the mole. The molecular mass and the formula mass of a compound are obtained by adding together the atomic masses of the atoms present in the molecular formula or empirical formula, respectively; the units of both are atomic mass units (amu). The mole is a unit used to measure the number of atoms, molecules, or (in the case of ionic compounds) formula units in a given mass of a substance. The mole is defined as the amount of substance that contains the number of carbon atoms in exactly 12 g of carbon-12, Avogadro's number (6.022×10^{23}) of atoms of carbon-12. The molar mass of a substance is defined as the mass of 1 mol of that substance, expressed in grams per mole, and is equal to the mass of 6.022×10^{23} atoms, molecules, or formula units of that substance.

Answers

Exercise 3.4.1: Molecular Mass of Freon

137.368 amu

Exercise 3.4.2: Formula Mass of Silicon Nitride

$140.29\ amu$

Exercise 3.4.4: Freon-11

0.546 mol

3.29×10^{23} molecules

Exercise 3.4.5

1.71 g

0.721 g

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3.5: Empirical Formulas from Analysis

Learning Objectives

- To understand the definition and difference between empirical formulas and chemical formulas
- To understand how combustion analysis can be used to identify chemical formulas

Chemical formulas tell you how many atoms of each element are in a compound, and empirical formulas tell you the simplest or most reduced ratio of elements in a compound. If a compound's chemical formula cannot be reduced any more, then the empirical formula is the same as the chemical formula. Combustion analysis can determine the empirical formula of a compound, but cannot determine the chemical formula (other techniques can though). Once known, the chemical formula can be calculated from the empirical formula.

Empirical Formulas

An empirical formula tells us the relative ratios of different atoms in a compound. The ratios hold true on the *molar* level as well. Thus, H_2O is composed of two atoms of hydrogen and 1 atom of oxygen. Likewise, **1.0 mole of H_2O** is composed **of 2.0 moles of hydrogen** and **1.0 mole of oxygen**. We can also work backwards from molar ratios since *if we know the molar amounts of each element in a compound we can determine the empirical formula*.

Example 3.5.1: Mercury Chloride

Mercury forms a compound with chlorine that is 73.9% mercury and 26.1% chlorine by mass. What is the empirical formula?

Solution

Let's say we had a 100 gram sample of this compound. The sample would therefore contain 73.9 grams of mercury and 26.1 grams of chlorine. How many moles of each atom do the individual masses represent?

For Mercury:

$$(73.9\ g) \times \left(\frac{1\ mol}{200.59\ g}\right) = 0.368\ moles$$

For Chlorine:

$$(26.1\ g) \times \left(\frac{1\ mol}{35.45\ g}\right) = 0.736\ mol$$

What is the molar ratio between the two elements?

$$\frac{0.736\ mol\ Cl}{0.368\ mol\ Hg} = 2.0$$

Thus, we have twice as many moles (i.e. atoms) of Cl as Hg. The empirical formula would thus be (remember to list cation first, anion last):

$$\mathrm{HgCl_2}$$

Chemical Formula from Empirical Formula

The chemical formula for a compound obtained by composition analysis is always the empirical formula. We can obtain the chemical formula from the empirical formula if we know the molecular weight of the compound. The chemical formula will always

be some *integer multiple* of the empirical formula (i.e. integer multiples of the subscripts of the empirical formula). The general flow for this approach is shown in Figure 3.5.1 and demonstrated in Example 3.5.2.

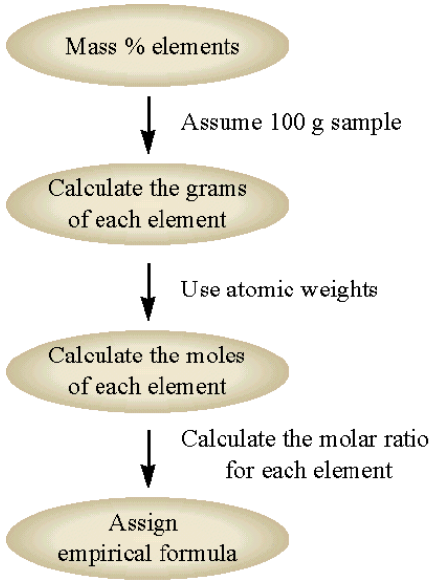


Figure 3.5.1: The general flow chart for solving empirical formulas from known mass percentages.

Flowchart. From mass % elements, calculate the grams of each element. Then, use atomic weights to calculate the moles of each element. Then, assign empirical formula by calculating the molar ratio for each element.

Example 3.5.2: Ascorbic Acid

Vitamin C (ascorbic acid) contains 40.92 % C, 4.58 % H, and 54.50 % O, by mass. The experimentally determined molecular mass is 176 amu. What is the empirical and chemical formula for ascorbic acid?

Solution

Consider an arbitrary amount of 100 grams of ascorbic acid, so we would have:

- 40.92 grams C
- 4.58 grams H
- 54.50 grams O

This would give us how many moles of each element?

- Carbon

$$(40.92\ \cancel{g\,C}) \times \left(\frac{1\ mol\ C}{12.011\ \cancel{g\,C}}\right) = 3.407\ mol\ C$$

- Hydrogen

$$(4.58\ \cancel{g\,H}) \times \left(\frac{1\ mol\ H}{1.008\ \cancel{g\,H}}\right) = 4.544\ mol\ H$$

- Oxygen

$$(54.50\ \cancel{g\,O}) \times \left(\frac{1\ mol\ O}{15.999\ \cancel{g\,O}}\right) = 3.406\ mol\ O$$

Determine the simplest whole number ratio by dividing by the smallest molar amount (3.406 moles in this case - see oxygen):

- Carbon

$$C = \frac{3.407\ mol}{3.406\ mol} \approx 1.0$$

- Hydrogen

$$C = \frac{4.544\ mol}{3.406\ mol} = 1.333$$

- Oxygen

$$C = \frac{3.406\ mol}{3.406\ mol} = 1.0$$

The relative molar amounts of carbon and oxygen appear to be equal, but the relative molar amount of hydrogen is higher. Since we cannot have "fractional" atoms in a compound, we need to normalize the relative amount of hydrogen to be equal to an integer. 1.333 would appear to be 1 and 1/3, so if we multiply the relative amounts of each atom by '3', we should be able to get integer values for each atom.

C = (1.0)*3 = 3

H = (1.333)*3 = 4

O = (1.0)*3 = 3

or

$$C_3H_4O_3$$

This is our ***empirical formula*** for ascorbic acid.

What about the chemical formula? We are told that the experimentally determined molecular mass is **176 *amu***. What is the molecular mass of our empirical formula?

(3*12.011) + (4*1.008) + (3*15.999) = 88.062 *amu*

The molecular mass from our empirical formula is significantly lower than the experimentally determined value. What is the ratio between the two values?

(176 *amu*/88.062 *amu*) = 2.0

Thus, it would appear that our empirical formula is essentially one half the mass of the actual molecular mass. If we multiplied our empirical formula by '2', then the molecular mass would be correct. Thus, the actual chemical formula is:

2* $C_3H_4O_3$ **= $C_6H_8O_6$**

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Empirical Formulas: Empirical Formulas, YouTube(opens in new window) [youtu.be]

Combustion Analysis

When a compound containing carbon and hydrogen is subject to combustion with oxygen in a special combustion apparatus all the carbon is converted to CO_2 and the hydrogen to H_2O (Figure 3.5.2). The amount of carbon produced can be determined by measuring the amount of CO_2 produced. This is trapped by the sodium hydroxide, and thus we can monitor the mass of CO_2 produced by determining the increase in mass of the CO_2 trap. Likewise, we can determine the amount of H produced by the amount of H_2O trapped by the magnesium perchlorate.

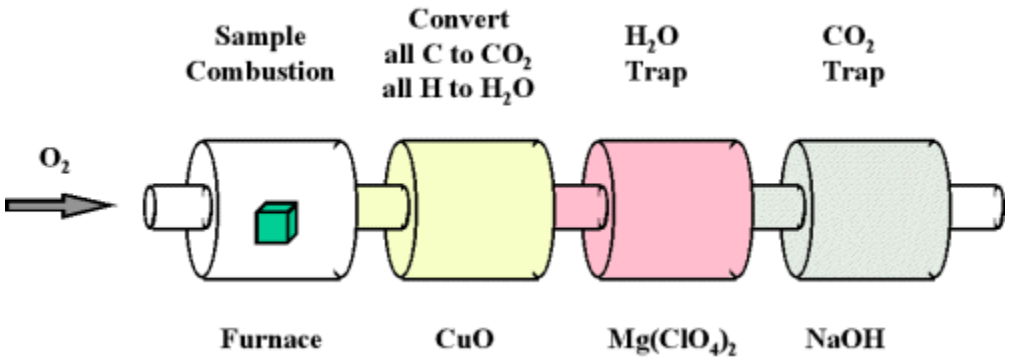


Figure 3.5.2: Combustion analysis apparatus

Diagram of a combustion chamber. O 2 enters the furnace and combusts the sample. All carbon is converted to C O 2 and all hydrogen is converted to H 2 O in the presence of C u O in the next chamber. The next chamber is an H 2 O trap with M g (C l O 4) 2 inside. The next chamber is a C O 2 trap with N a O H inside.

One of the most common ways to determine the elemental composition of an unknown hydrocarbon is an analytical procedure called combustion analysis. A small, carefully weighed sample of an unknown compound that may contain carbon, hydrogen, nitrogen, and/or sulfur is burned in an oxygen atmosphere,Other elements, such as metals, can be determined by other methods. and the quantities of the resulting gaseous products (CO_2, H_2O, N_2, and SO_2, respectively) are determined by one of several possible methods. One procedure used in combustion analysis is outlined schematically in Figure 3.5.3 and a typical combustion analysis is illustrated in Examples 3.5.3 and 3.5.4.

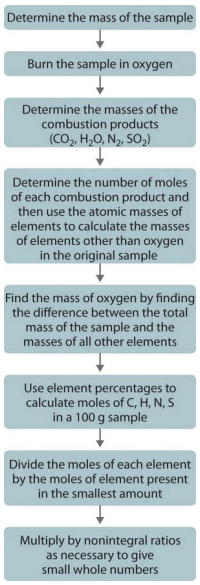


Figure 3.5.3: Steps for Obtaining an Empirical Formula from Combustion Analysis. (CC BY-NC-SA; anonymous)

Example 3.5.3: Combustion of Isopropyl Alcohol

What is the empirical formulate for isopropyl alcohol (which contains only C, H and O) if the combustion of a 0.255 grams isopropyl alcohol sample produces 0.561 grams of CO_2 and 0.306 grams of H_2O?

Solution

From this information quantitate the amount of C and H in the sample.

$$(0.561\ \cancel{g\ CO_2}) \left(\frac{1\ mol\ CO_2}{44.0\ \cancel{g\ CO_2}} \right) = 0.0128\ mol\ CO_2$$

Since one mole of CO_2 is made up of one mole of C and two moles of O, if we have 0.0128 moles of CO_2 in our sample, then we know we have 0.0128 moles of C in the sample. How many grams of C is this?

$$(0.0128\ \cancel{mol\ C}) \left(\frac{12.011\ g\ C}{1\ \cancel{mol\ C}} \right) = 0.154\ g\ C$$

How about the hydrogen?

$$(0.306\ \cancel{g\ H_2O}) \left(\frac{1\ mol\ H_2O}{18.0\ \cancel{g\ H_2O}} \right) = 0.017\ mol\ H_2O$$

Since one mole of H_2O is made up of one mole of oxygen and ***two*** moles of hydrogen, if we have 0.017 moles of H_2O, then we have 2*(0.017) = 0.034 moles of hydrogen. Since hydrogen is about 1 gram/mole, we must have **0.034 grams of hydrogen** in our original sample.

When we add our carbon and hydrogen together we get:

0.154 grams (C) + 0.034 grams (H) = **0.188 grams**

But we know we combusted *0.255 grams* of isopropyl alcohol. The 'missing' mass must be from the oxygen atoms in the isopropyl alcohol:

0.255 grams - 0.188 grams = 0.067 grams oxygen

This much oxygen is how many moles?

$$(0.067\ \cancel{g O})\left(\frac{1\ mol\ O}{15.994\ \cancel{g O}}\right) = 0.0042\ mol\ O$$

Overall therefore, we have:

- 0.0128 moles Carbon
- 0.0340 moles Hydrogen
- 0.0042 moles Oxygen

Divide by the smallest molar amount to normalize:

- C = 3.05 atoms
- H = 8.1 atoms
- O = 1 atom

Within experimental error, the most likely empirical formula for propanol would be C_3H_8O

Example 3.5.4: Combustion of Naphalene

Naphthalene, the active ingredient in one variety of mothballs, is an organic compound that contains carbon and hydrogen only. Complete combustion of a 20.10 mg sample of naphthalene in oxygen yielded 69.00 mg of CO_2 and 11.30 mg of H_2O. Determine the empirical formula of naphthalene.

Given: mass of sample and mass of combustion products

Asked for: empirical formula

Strategy:

A. Use the masses and molar masses of the combustion products, CO_2 and H_2O, to calculate the masses of carbon and hydrogen present in the original sample of naphthalene.
B. Use those masses and the molar masses of the elements to calculate the empirical formula of naphthalene.

Solution:

A Upon combustion, 1 mol of CO_2 is produced for each mole of carbon atoms in the original sample. Similarly, 1 mol of H_2O is produced for every 2 mol of hydrogen atoms present in the sample. The masses of carbon and hydrogen in the original sample can be calculated from these ratios, the masses of CO_2 and H_2O, and their molar masses. Because the units of molar mass are grams per mole, we must first convert the masses from milligrams to grams:

$$mass\ of\ C = 69.00\,mg\,CO_2 \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,CO_2}{44.010\,g\,CO_2} \times \frac{1\,molC}{1\,mol\,CO_2} \times \frac{12.011\,g}{1\,mol\,C}$$

$$= 1.883 \times 10^{-2}\,g\,C$$

$$mass\ of\ H = 11.30\,mg\,H_2O \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,H_2O}{18.015\,g\,H_2O} \times \frac{2\,molH}{1\,mol\,H_2O} \times \frac{1.0079\,g}{1\,mol\,H}$$

$$= 1.264 \times 10^{-3}\,g\,H$$

B To obtain the relative numbers of atoms of both elements present, we need to calculate the number of moles of each and divide by the number of moles of the element present in the smallest amount:

$$moles\,C = 1.883 \times 10^{-2}\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 1.568 \times 10^{-3}\,molC$$

$$moles\ H = 1.264 \times 10^{-3}\ g\ H \times \frac{1\ mol\ H}{1.0079\ g\ H} = 1.254 \times 10^{-3}\ mol H$$

Dividing each number by the number of moles of the element present in the smaller amount gives

$$H: \frac{1.254 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.000 \quad C: \frac{1.568 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.250$$

Thus naphthalene contains a 1.25:1 ratio of moles of carbon to moles of hydrogen: $C_{1.25}H_{1.0}$. Because the ratios of the elements in the empirical formula must be expressed as small whole numbers, multiply both subscripts by 4, which gives C_5H_4 as the empirical formula of naphthalene. In fact, the chemical formula of naphthalene is $C_{10}H_8$, which is consistent with our results.

Exercise 3.5.4

a. Xylene, an organic compound that is a major component of many gasoline blends, contains carbon and hydrogen only. Complete combustion of a 17.12 mg sample of xylene in oxygen yielded 56.77 mg of CO_2 and 14.53 mg of H_2O. Determine the empirical formula of xylene.
b. The empirical formula of benzene is CH (its chemical formula is C_6H_6). If 10.00 mg of benzene is subjected to combustion analysis, what mass of CO_2 and H_2O will be produced?

Answer a available at the end of this section.

YouTube Video

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Combustion Analysis: Combustion Analysis, YouTube(opens in new window) [youtu.be]

Answers

Exercise 3.5.4

The empirical formula is C_4H_5. (The chemical formula of xylene is actually C_8H_{10}.)

33.81 mg of CO_2; 6.92 mg of H_2O

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3.6: Quantitative Information from Balanced Equations

Learning Objectives

- To balance equations that describe reactions in solution.
- To calculate the quantities of compounds produced or consumed in a chemical reaction.
- To solve quantitative problems involving the stoichiometry of reactions in solution.

A balanced chemical equation gives the identity of the reactants and the products as well as the accurate number of molecules or moles of each that are consumed or produced. **Stoichiometry** is a collective term for the quantitative relationships between the masses, the numbers of moles, and the numbers of particles (atoms, molecules, and ions) of the reactants and the products in a balanced chemical equation. **A stoichiometric quantity** is the amount of product or reactant specified by the coefficients in a balanced chemical equation. This section describes how to use the stoichiometry of a reaction to answer questions like the following: How much oxygen is needed to ensure complete combustion of a given amount of isooctane? (This information is crucial to the design of nonpolluting and efficient automobile engines.) How many grams of pure gold can be obtained from a ton of low-grade gold ore? (The answer determines whether the ore deposit is worth mining.) If an industrial plant must produce a certain number of tons of sulfuric acid per week, how much elemental sulfur must arrive by rail each week?

All these questions can be answered using the concepts of the mole, molar and formula masses, and solution concentrations, along with the coefficients in the appropriate balanced chemical equation.

Stoichiometry Problems

When carrying out a reaction in either an industrial setting or a laboratory, it is easier to work with masses of substances than with the numbers of molecules or moles. The general method for converting from the mass of any reactant or product to the mass of any other reactant or product using a balanced chemical equation is outlined in and described in the following text.

Steps in Converting between Masses of Reactant and Product

1. Convert the mass of one substance (substance A) to the corresponding number of moles using its molar mass.
2. From the balanced chemical equation, obtain the number of moles of another substance (B) from the number of moles of substance A using the appropriate mole ratio (the ratio of their coefficients).
3. Convert the number of moles of substance B to mass using its molar mass. It is important to remember that some species are present in excess by virtue of the reaction conditions. For example, if a substance reacts with the oxygen in air, then oxygen is in obvious (but unstated) excess.

Converting amounts of substances to moles—and vice versa—is the key to all stoichiometry problems, whether the amounts are given in units of mass (grams or kilograms), weight (pounds or tons), or volume (liters or gallons).

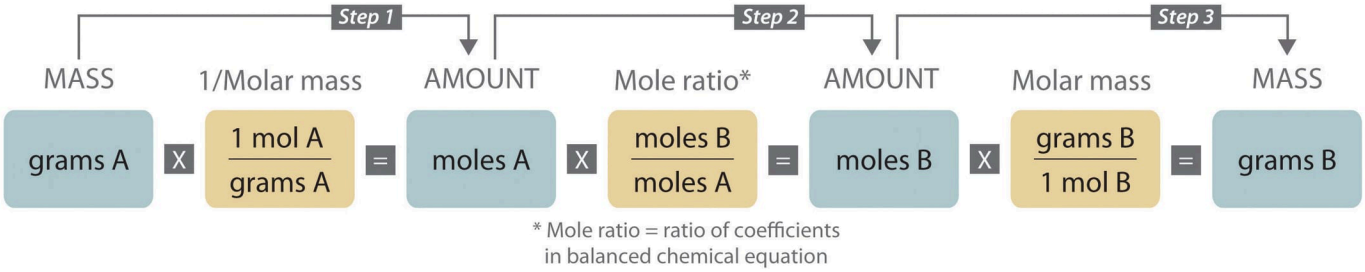


Figure 3.6.1: A Flowchart for Stoichiometric Calculations Involving Pure Substances. The molar masses of the reactants and the products are used as conversion factors so that you can calculate the mass of product from the mass of reactant and vice versa.

Flowchart of steps in stoichiometric calculations. Step 1: grams of A is converted to moles by multiplying by the inverse of the molar mass. Step 2: moles of A is converted to moles of B by multiplying by the molar ratio. Step 3: moles of B is converted to grams of B by the molar mass.

To illustrate this procedure, consider the combustion of glucose. Glucose reacts with oxygen to produce carbon dioxide and water:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \tag{3.6.1}$$

Just before a chemistry exam, suppose a friend reminds you that glucose is the major fuel used by the human brain. You therefore decide to eat a candy bar to make sure that your brain does not run out of energy during the exam (even though there is no direct evidence that consumption of candy bars improves performance on chemistry exams). If a typical 2 oz candy bar contains the equivalent of 45.3 g of glucose and the glucose is completely converted to carbon dioxide during the exam, how many grams of carbon dioxide will you produce and exhale into the exam room?

The initial step in solving a problem of this type is to write the balanced chemical equation for the reaction. Inspection shows that it is balanced as written, so the strategy outlined above can be adapted as follows:

1. Use the molar mass of glucose (to one decimal place, 180.2 g/mol) to determine the number of moles of glucose in the candy bar:

$$moles\,glucose = 45.3\,g\,glucose \times \frac{1\,mol\,glucose}{180.2\,g\,glucose} = 0.251\,mol\,glucose$$

2. According to the balanced chemical equation, 6 mol of CO_2 is produced per mole of glucose; the mole ratio of CO_2 to glucose is therefore 6:1. The number of moles of CO_2 produced is thus

$$moles\,CO_2 = mol\,glucose \times \frac{6\,mol\,CO_2}{1\,mol\,glucose}$$

$$= 0.251\,mol\,glucose \times \frac{6\,mol\,CO_2}{1\,mol\,glucose}$$

$$= 1.51\,mol\,CO_2$$

3. Use the molar mass of CO_2 (44.010 g/mol) to calculate the mass of CO_2 corresponding to 1.51 mol of CO_2:

$$mass\,of\,CO_2 = 1.51\,mol\,CO_2 \times \frac{44.010\,g\,CO_2}{1\,mol\,CO_2} = 66.5\,g\,CO_2$$

These operations can be summarized as follows:

$$45.3\,g\,glucose \times \frac{1\,mol\,glucose}{180.2\,g\,glucose} \times \frac{6\,mol\,CO_2}{1\,mol\,glucose} \times \frac{44.010\,g\,CO_2}{1\,mol\,CO_2} = 66.4\,g\,CO_2$$

Discrepancies between the two values are attributed to rounding errors resulting from using stepwise calculations in steps 1–3. (Remember that you should generally carry extra significant digits through a multistep calculation to the end to avoid this!) This amount of gaseous carbon dioxide occupies an enormous volume—more than 33 L. Similar methods can be used to calculate the amount of oxygen consumed or the amount of water produced.

The balanced chemical equation was used to calculate the mass of product that is formed from a certain amount of reactant. It can also be used to determine the masses of reactants that are necessary to form a certain amount of product or, as shown in Example 3.6.1, the mass of one reactant that is required to consume a given mass of another reactant.

Example 3.6.1: The US Space Shuttle

The combustion of hydrogen with oxygen to produce gaseous water is extremely vigorous, producing one of the hottest flames known. Because so much energy is released for a given mass of hydrogen or oxygen, this reaction was used to fuel the NASA (National Aeronautics and Space Administration) space shuttles, which have recently been retired from service. NASA engineers calculated the exact amount of each reactant needed for the flight to make sure that the shuttles did not carry excess fuel into orbit. Calculate how many tons of hydrogen a space shuttle needed to carry for each 1.00 tn of oxygen (1 tn = 2000 lb).



The US space shuttle Discovery during liftoff. *The large cylinder in the middle contains the oxygen and hydrogen that fueled the shuttle's main engine.*

Given: reactants, products, and mass of one reactant

Asked for: mass of other reactant

Strategy:

A. Write the balanced chemical equation for the reaction.
B. Convert mass of oxygen to moles. From the mole ratio in the balanced chemical equation, determine the number of moles of hydrogen required. Then convert the moles of hydrogen to the equivalent mass in tons.

Solution:

We use the same general strategy for solving stoichiometric calculations as in the preceding example. Because the amount of oxygen is given in tons rather than grams, however, we also need to convert tons to units of mass in grams. Another conversion is needed at the end to report the final answer in tons.

A We first use the information given to write a balanced chemical equation. Because we know the identity of both the reactants and the product, we can write the reaction as follows:

$$H_2(g) + O_2(g) \rightarrow H_2O(g)$$

This equation is not balanced because there are two oxygen atoms on the left side and only one on the right. Assigning a coefficient of 2 to both H_2O and H_2 gives the balanced chemical equation:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Thus 2 mol of H_2 react with 1 mol of O_2 to produce 2 mol of H_2O.

1. **B** To convert tons of oxygen to units of mass in grams, we multiply by the appropriate conversion factors:

$$mass\,of\,O_2 = 1.00\,tn \times \frac{2000\,lb}{tn} \times \frac{453.6\,g}{lb} = 9.07 \times 10^5\,g\,O_2$$

Using the molar mass of O_2 (32.00 g/mol, to four significant figures), we can calculate the number of moles of O_2 contained in this mass of O_2:

$$mol\,O_2 = 9.07 \times 10^5\,g\,O_2 \times \frac{1\,mol\,O_2}{32.00\,g\,O_2} = 2.83 \times 10^4\,mol\,O_2$$

2. Now use the coefficients in the balanced chemical equation to obtain the number of moles of H_2 needed to react with this number of moles of O_2:

$$mol\,H_2 = mol\,O_2 \times \frac{2\,mol\,H_2}{1\,mol\,O_2}$$

$$= 2.83 \times 10^4\,mol\,O_2 \times \frac{2\,mol\,H_2}{1\,mol\,O_2} = 5.66 \times 10^4\,mol\,H_2$$

3. The molar mass of H_2 (2.016 g/mol) allows us to calculate the corresponding mass of H_2:

$$mass\,of\,H_2 = 5.66 \times 10^4\,mol\,H_2 \times \frac{2.016\,g\,H_2}{mol\,H_2} = 1.14 \times 10^5\,g\,H_2$$

Finally, convert the mass of H2 to the desired units (tons) by using the appropriate conversion factors:

$$tons\,H_2 = 1.14 \times 10^5\,g\,H_2 \times \frac{1\,lb}{453.6\,g} \times \frac{1\,tn}{2000\,lb} = 0.126\,tn\,H_2$$

The space shuttle had to be designed to carry 0.126 tn of H_2 for each 1.00 tn of O_2. Even though 2 mol of H_2 are needed to react with each mole of O_2, the molar mass of H_2 is so much smaller than that of O_2 that only a relatively small mass of H_2 is needed compared to the mass of O_2.

Exercise 3.6.1: Roasting Cinnabar

Cinnabar, (or Cinnabarite) HgS is the common ore of mercury. Because of its mercury content, cinnabar can be toxic to human beings; however, because of its red color, it has also been used since ancient times as a pigment.



Cinnabar ore. from Wikipedia

Alchemists produced elemental mercury by roasting cinnabar ore in air:

$$HgS(s) + O_2(g) \rightarrow Hg(l) + SO_2(g)$$

The volatility and toxicity of mercury make this a hazardous procedure, which likely shortened the life span of many alchemists. Given 100 g of cinnabar, how much elemental mercury can be produced from this reaction?

Answer available at the end of this section.

Calculating Moles from Volume

Quantitative calculations involving reactions in solution are carried out with *masses*, however, *volumes* of solutions of known concentration are used to determine the number of moles of reactants. Whether dealing with volumes of solutions of reactants or masses of reactants, the coefficients in the balanced chemical equation give the number of moles of each reactant needed and the number of moles of each product that can be produced. An expanded version of the flowchart for stoichiometric calculations is shown in Figure 3.6.2. The balanced chemical equation for the reaction and *either* the masses of solid reactants and products *or* the volumes of solutions of reactants and products can be used to determine the amounts of other species, as illustrated in the following examples.

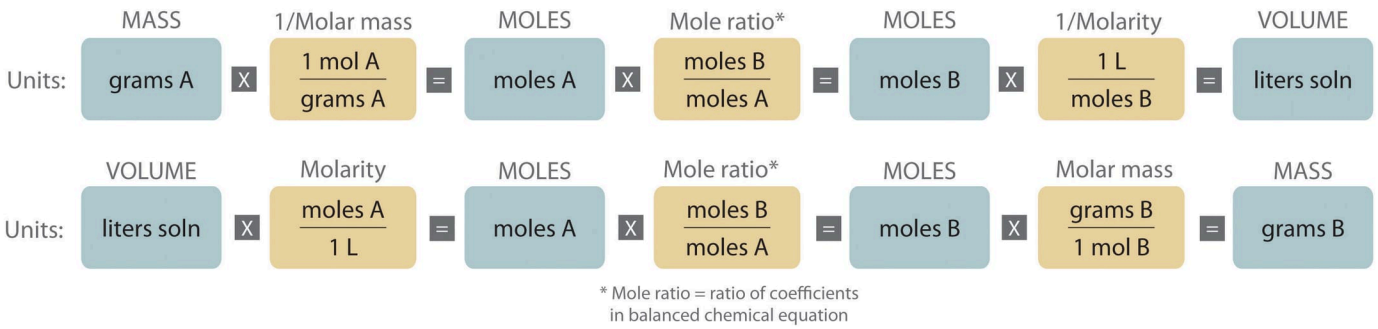


Figure 3.6.2: An Expanded Flowchart for Stoichiometric Calculations. Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in a balanced chemical equation.

Top: flowchart of steps to convert mass of one substance to moles to moles of another substance to volume using molarity. Bottom: flowchart of steps to convert volume of a substance to mass of another substance.

The balanced chemical equation for a reaction and either the masses of solid reactants and products or the volumes of solutions of reactants and products can be used in stoichiometric calculations.

Example 3.6.2 : Extraction of Gold

Gold is extracted from its ores by treatment with an aqueous cyanide solution, which causes a reaction that forms the soluble $[Au(CN)_2]^-$ ion. Gold is then recovered by reduction with metallic zinc according to the following equation:

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

What mass of gold can be recovered from 400.0 L of a 3.30×10^{-4} M solution of $[Au(CN)_2]^-$?

Given: chemical equation and molarity and volume of reactant

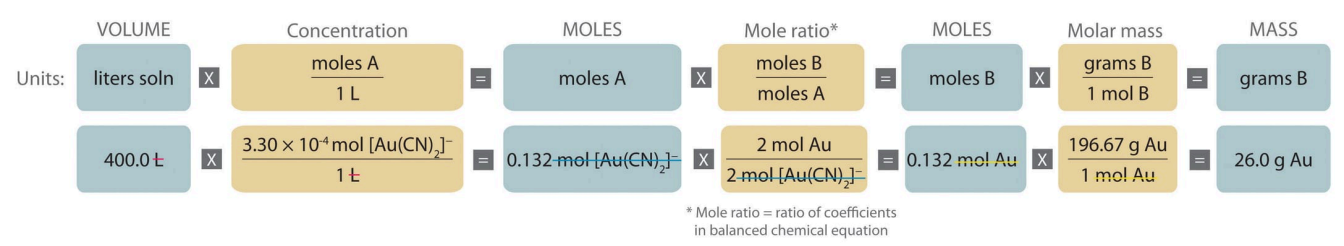
Asked for: mass of product

Strategy:

A. Check the chemical equation to make sure it is balanced as written; balance if necessary. Then calculate the number of moles of $[Au(CN)_2]^-$ present by multiplying the volume of the solution by its concentration.
B. From the balanced chemical equation, use a mole ratio to calculate the number of moles of gold that can be obtained from the reaction. To calculate the mass of gold recovered, multiply the number of moles of gold by its molar mass.

Solution:

A The equation is balanced as written; proceed to the stoichiometric calculation. Figure 3.6.2 is adapted for this particular problem as follows:



Flowchart. Top: volume is converted to moles of A via the concentration. Moles of A is then converted to moles of B via the mole ratio. The molar mass of B is then used to convert moles of B to grams. Bottom: same flowchart as above, filled in with information given in the exercise.

As indicated in the strategy, start by calculating the number of moles of $[Au(CN)_2]^-$ present in the solution from the volume and concentration of the $[Au(CN)_2]^-$ solution:

$$moles\ [Au(CN)_2]^- = V_L M_{mol/L} \tag{3.6.2}$$

$$= 400.0\ \cancel{L}\left(\frac{3.30 \times 10^{4-}\ mol\ [Au(CN)_2]^-}{1\ \cancel{L}}\right) = 0.132\ mol\ [Au(CN)_2]^- \tag{3.6.3}$$

B Because the coefficients of gold and the $[Au(CN)_2]^-$ ion are the same in the balanced chemical equation, assuming that Zn(s) is present in excess, the number of moles of gold produced is the same as the number of moles of $[Au(CN)_2]^-$ (i.e., 0.132 mol of Au). The problem asks for the mass of gold that can be obtained, so the number of moles of gold must be converted to the corresponding mass using the molar mass of gold:

$$mass\ of\ Au = (moles\ Au)(molar\ mass\ Au) \tag{3.6.4}$$

$$= 0.132\ \cancel{mol\ Au}\left(\frac{196.97\ g\ Au}{1\ \cancel{mol\ Au}}\right) = 26.0\ g\ Au \tag{3.6.5}$$

At a 2011 market price of over $1400 per troy ounce (31.10 g), this amount of gold is worth $1170.

$$26.0\ \cancel{g\ Au} \times \frac{1\ \cancel{troy\ oz}}{31.10\ \cancel{g}} \times \frac{\$1400}{1\ \cancel{troy\ oz\ Au}} = \$1170$$

Exercise 3.6.2 : Lanthanum Oxalate

What mass of solid lanthanum(III) oxalate nonahydrate $[La_2(C_2O_4)_3{\bullet}9H_2O]$ can be obtained from 650 mL of a 0.0170 M aqueous solution of $LaCl_3$ by adding a stoichiometric amount of sodium oxalate?

Answer available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors (Mol Ratios): Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors, YouTube(opens in new window) [youtu.be]

Summary

Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in the balanced chemical equation. Quantitative calculations that involve the stoichiometry of reactions in solution use volumes of solutions of known concentration instead of masses of reactants or products. The coefficients in the balanced chemical equation tell how many moles of reactants are needed and how many moles of product can be produced.

Answers

Exercise 3.6.1**: Roasting Cinnabar**

86.2 g

Exercise 3.6.2 **: Lanthanum Oxalate**

3.89 g

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3.7: Limiting Reactants

Learning Objectives

- To understand the concept of limiting reactants and quantify incomplete reactions

In all the examples discussed thus far, the reactants were assumed to be present in stoichiometric quantities. Consequently, none of the reactants was left over at the end of the reaction. This is often desirable, as in the case of a space shuttle, where excess oxygen or hydrogen was not only extra freight to be hauled into orbit but also an explosion hazard. More often, however, reactants are present in mole ratios that are not the same as the ratio of the coefficients in the balanced chemical equation. As a result, one or more of them will not be used up completely but will be left over when the reaction is completed. In this situation, the amount of product that can be obtained is limited by the amount of only one of the reactants. The reactant that restricts the amount of product obtained is called the limiting reactant. The reactant that remains after a reaction has gone to completion is in excess.

Consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is thus

$$1\,\text{box mix} + 2\,\text{eggs} \rightarrow 1\,\text{batch brownies} \tag{3.7.1}$$

If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes in is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant. Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

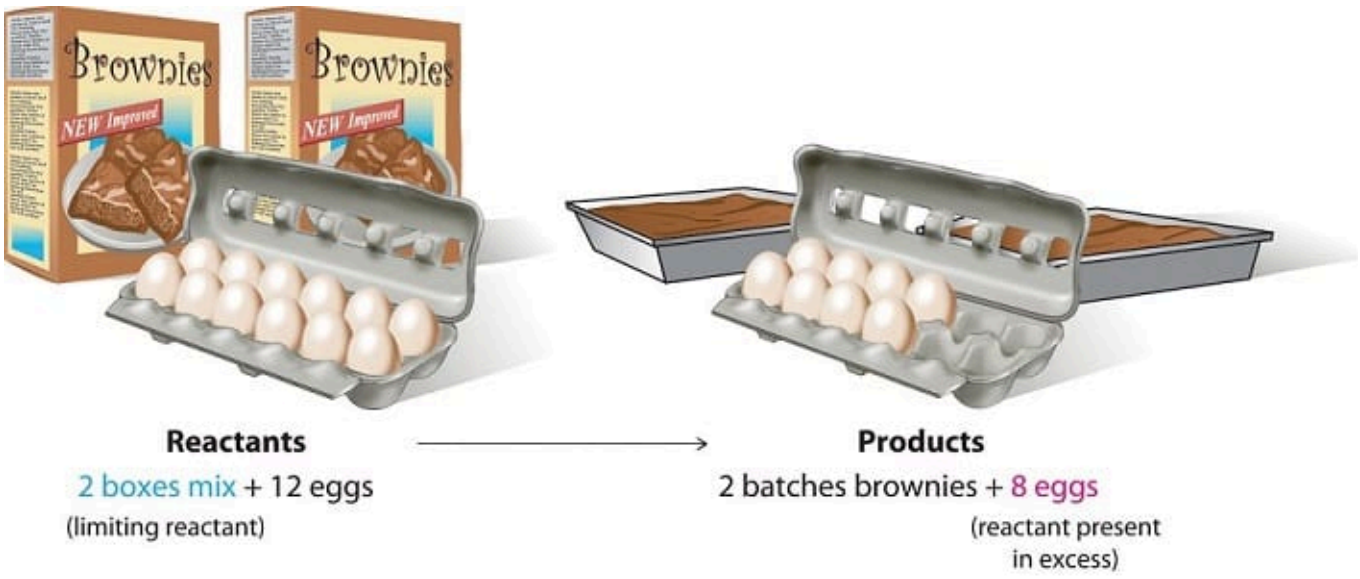


Figure 3.7.1: The Concept of a Limiting Reactant in the Preparation of Brownies

Reactants: 2 boxes of brownie mix + 12 eggs produces 2 batches of brownies + 8 eggs. Brownie mix is the limiting reactant. Eggs are the reactant present in excess.

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Introduction to Limiting Reactant Problems: Introduction to Limiting Reactant Problems, YouTube(opens in new window) [youtu.be]

Now consider a chemical example of a limiting reactant: the production of pure titanium. This metal is fairly light (45% lighter than steel and only 60% heavier than aluminum) and has great mechanical strength (as strong as steel and twice as strong as aluminum). Because it is also highly resistant to corrosion and can withstand extreme temperatures, titanium has many applications in the aerospace industry. Titanium is also used in medical implants and portable computer housings because it is light and resistant to corrosion. Although titanium is the ninth most common element in Earth's crust, it is relatively difficult to extract from its ores. In the first step of the extraction process, titanium-containing oxide minerals react with solid carbon and chlorine gas to form titanium tetrachloride ($\mathrm{TiCl_4}$) and carbon dioxide.

$$\mathrm{TiO_2\,(s) + Cl_2\,(g)\ \rightarrow TiCl_4\,(g) + CO_2\,(g)}$$

Titanium tetrachloride is then converted to metallic titanium by reaction with molten magnesium metal at high temperature:

$$\mathrm{TiCl_4\,(g) + 2\ Mg\,(l)\ \rightarrow Ti\,(s) + 2\ MgCl_2\,(l)} \tag{3.7.2}$$

Because titanium ores, carbon, and chlorine are all rather inexpensive, the high price of titanium (about $100 per kilogram) is largely due to the high cost of magnesium metal. Under these circumstances, magnesium metal is the limiting reactant in the production of metallic titanium.



Figure 3.7.2: Medical use of titanium. Here is an example of its successful use in joint replacement implants. An A-P X-ray of a pelvis showing a total hip joint replacement. The right hip joint (on the left in the photograph) has been replaced. A metal prostheses is cemented in the top of the right femur and the head of the femur has been replaced by the rounded head of the prosthesis. Figure courtesy of NIH (NIADDK) 9AO4 (Connie Raab)

With 1.00 kg of titanium tetrachloride and 200 g of magnesium metal, how much titanium metal can be produced according to

Equation 3.7.2?

Solving this type of problem requires that you carry out the following steps

1. Determine the number of moles of each reactant.
2. Compare the mole ratio of the reactants with the ratio in the balanced chemical equation to determine which reactant is limiting.
3. Calculate the number of moles of product that can be obtained from the limiting reactant.
4. Convert the number of moles of product to mass of product.

Step 1: To determine the number of moles of reactants present, calculate or look up their molar masses: 189.679 g/mol for titanium tetrachloride and 24.305 g/mol for magnesium. The number of moles of each is calculated as follows:

$$\begin{aligned}\text{moles } \mathrm{TiCl_4} &= \frac{\text{mass } \mathrm{TiCl_4}}{\text{molar mass } \mathrm{TiCl_4}} \\ &= 1000 \,\cancel{g}\ \mathrm{TiCl_4} \times \frac{1\, mol\ TiCl_4}{189.679\ \cancel{g}\ \mathrm{TiCl_4}} \\ &= 5.272\, mol\ \mathrm{TiCl_4} \end{aligned} \tag{3.7.3}$$

$$\begin{aligned}\text{moles } \mathrm{Mg} &= \frac{\text{mass } \mathrm{Mg}}{\text{molar mass } \mathrm{Mg}} \\ &= 200 \,\cancel{g}\ \mathrm{Mg} \times \frac{1\ mol\,\mathrm{Mg}}{24.305\ \cancel{g}\ \mathrm{Mg}} \\ &= 8.23\,\mathrm{mol\ Mg} \end{aligned} \tag{3.7.4}$$

Step 2: There are more moles of magnesium than of titanium tetrachloride, but the ratio is only the following:

$$\frac{mol\,\mathrm{Mg}}{mol\,\mathrm{TiCl_4}} = \frac{8.23\, mol}{5.272\, mol} = 1.56$$

Because the ratio of the coefficients in the balanced chemical equation is,

$$\frac{2\, mol\,\mathrm{Mg}}{1\, mol\,\mathrm{TiCl_4}} = 2$$

there is not have enough magnesium to react with all the titanium tetrachloride. If this point is not clear from the mole ratio, calculate the number of moles of one reactant that is required for complete reaction of the other reactant. For example, there are 8.23 mol of Mg, so (8.23 ÷ 2) = 4.12 mol of $\mathrm{TiCl_4}$ are required for complete reaction. Because there are 5.272 mol of $\mathrm{TiCl_4}$, titanium tetrachloride is present in excess. Conversely, 5.272 mol of $\mathrm{TiCl_4}$ requires 2 × 5.272 = 10.54 mol of Mg, but there are only 8.23 mol. Therefore, magnesium is the limiting reactant.

Step 3: Because magnesium is the limiting reactant, the number of moles of magnesium determines the number of moles of titanium that can be formed:

$$mol\ \mathrm{Ti} = 8.23\, mol\ \mathrm{Mg} = \frac{1\, mol\ \mathrm{Ti}}{2\, mol\ \mathrm{Mg}} = 4.12\, mol\ \mathrm{Ti}$$

Thus only 4.12 mol of Ti can be formed.

Step 4. To calculate the mass of titanium metal that can obtain, multiply the number of moles of titanium by the molar mass of titanium (47.867 g/mol):

$$\begin{aligned}\text{moles } \mathrm{Ti} &= \text{mass } \mathrm{Ti} \times \text{molar mass } \mathrm{Ti} \\ &= 4.12\, mol\ \mathrm{Ti} \times \frac{47.867\, g\ \mathrm{Ti}}{1\, mol\ \mathrm{Ti}} \\ &= 197\, g\ \mathrm{Ti}\end{aligned}$$

Here is a simple and reliable way to identify the limiting reactant in any problem of this sort:

1. Calculate the number of moles of each reactant present: 5.272 mol of $\mathrm{TiCl_4}$ and 8.23 mol of Mg.
2. Divide the actual number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation:

$$TiCl_4 : \frac{5.272\,mol\,(actual)}{1\,mol\,(stoich)} = 5.272$$

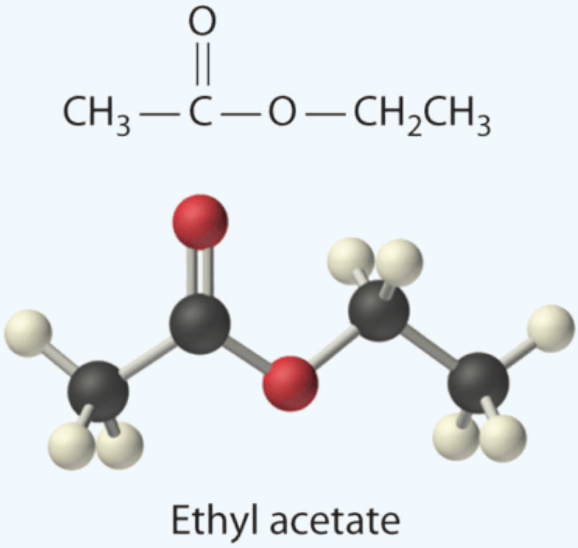
$$Mg : \frac{8.23\,mol\,(actual)}{2\,mol\,(stoich)} = 4.12$$

3. The reactant with the smallest mole ratio is limiting. Magnesium, with a calculated stoichiometric mole ratio of 4.12, is the limiting reactant.

Density is the mass per unit volume of a substance. If we are given the density of a substance, we can use it in stoichiometric calculations involving liquid reactants and/or products, as Example 3.7.1 demonstrates.

Example 3.7.1: Fingernail Polish Remover

Ethyl acetate ($CH_3CO_2C_2H_5$) is the solvent in many fingernail polish removers and is used to decaffeinate coffee beans and tea leaves. It is prepared by reacting ethanol (C_2H_5OH) with acetic acid (CH_3CO_2H); the other product is water. A small amount of sulfuric acid is used to accelerate the reaction, but the sulfuric acid is not consumed and does not appear in the balanced chemical equation. Given 10.0 mL each of acetic acid and ethanol, how many grams of ethyl acetate can be prepared from this reaction? The densities of acetic acid and ethanol are 1.0492 g/mL and 0.7893 g/mL, respectively.



Given: reactants, products, and volumes and densities of reactants

Asked for: mass of product

Strategy:

A. Balance the chemical equation for the reaction.
B. Use the given densities to convert from volume to mass. Then use each molar mass to convert from mass to moles.
C. Using mole ratios, determine which substance is the limiting reactant. After identifying the limiting reactant, use mole ratios based on the number of moles of limiting reactant to determine the number of moles of product.
D. Convert from moles of product to mass of product.

Solution:

A Always begin by writing the balanced chemical equation for the reaction:

$$C_2H_5OH\,(l) + CH_3CO_2H\,(aq) \rightarrow CH_3CO_2C_2H_5\,(aq) + H_2O\,(l)$$

B We need to calculate the number of moles of ethanol and acetic acid that are present in 10.0 mL of each. Recall that the density of a substance is the mass divided by the volume:

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

Rearranging this expression gives mass = (density)(volume). We can replace mass by the product of the density and the volume to calculate the number of moles of each substance in 10.0 mL (remember, 1 mL = 1 cm^3):

$$\begin{aligned}
\text{moles } C_2H_5OH &= \frac{\text{mass } C_2H_5OH}{\text{molar mass } \ C_2H_5OH} \\
&= \frac{(\text{volume } C_2H_5OH) \times (\text{density } C_2H_5OH)}{\text{molar mass } \ C_2H_5OH} \\
&= 10.0 \cancel{ml}\ {}_2CH_5OH \times \frac{0.7893 \cancel{g}\ C_2H_5OH}{1 \cancel{ml}\ C_2H_5OH} \times \frac{1\,mol\ C_2H_5OH}{46.07 \cancel{g}\ C_2H_5OH} \\
&= 0.171\,mol\ {}_2CH_5OH \\
\text{moles } CH_3CO_2H &= \frac{\text{mass } CH_3CO_2H}{\text{molar mass } CH_3CO_2H} \\
&= \frac{(\text{volume } CH_3CO_2H) \times (\text{density } CH_3CO_2H)}{\text{molar mass } CH_3CO_2H} \\
&= 10.0 \cancel{ml}\ CH_3CO_2H \times \frac{1.0492 \cancel{g}\ CH_3CO_2H}{1 \cancel{ml}\ CH_3CO_2H} \times \frac{1\,mol\ CH_3CO_2H}{60.05 \cancel{g}\ CH_3CO_2H} \\
&= 0.175\,mol\ CH_3CO_2H
\end{aligned}$$

C The number of moles of acetic acid exceeds the number of moles of ethanol. Because the reactants both have coefficients of 1 in the balanced chemical equation, the mole ratio is 1:1. We have 0.171 mol of ethanol and 0.175 mol of acetic acid, so ethanol is the limiting reactant and acetic acid is in excess. The coefficient in the balanced chemical equation for the product (ethyl acetate) is also 1, so the mole ratio of ethanol and ethyl acetate is also 1:1. This means that given 0.171 mol of ethanol, the amount of ethyl acetate produced must also be 0.171 mol:

$$\begin{aligned}
moles \text{ ethyl acetate} &= mol \text{ ethanol} \times \frac{1\,mol \text{ ethyl acetate}}{1\,mol \text{ ethanol}} \\
&= 0.171\,mol\ {}_2CH_5OH \times \frac{1\,mol\ CH_3CO_2C_2H_5}{1\,mol\ C_2H_5OH} \\
&= 0.171\,mol\ {}_{322}CHCOCH_5
\end{aligned}$$

D The final step is to determine the mass of ethyl acetate that can be formed, which we do by multiplying the number of moles by the molar mass:

$$\begin{aligned}
\text{mass of ethyl acetate} &= mol \text{ ethyl acetate} \times \text{molar mass ethyl acetate} \\
&= 0.171\,mol\ {}_{322}CHCOCH_5 \times \frac{88.11\,g\,CH_3CO_2C_2H_5}{1\,mol\,CH_3CO_2C_2H_5} \\
&= 15.1\,g\,CH_3CO_2C_2H_5
\end{aligned}$$

Thus 15.1 g of ethyl acetate can be prepared in this reaction. If necessary, you could use the density of ethyl acetate (0.9003 g/cm3) to determine the volume of ethyl acetate that could be produced:

$$\text{volume of ethyl acetate} = 15.1\,g\,CH_3CO_2C_2H_5 \times \frac{1\,ml\ CH_3CO_2C_2H_5}{0.9003\,g\ CH_3CO_2C_2H_5}$$

$$= 16.8\,ml\ {}_{322}CHCOCH_5$$

Exercise 3.7.1

Under appropriate conditions, the reaction of elemental phosphorus and elemental sulfur produces the compound P_4S_{10}. How much P_4S_{10} can be prepared starting with 10.0 g of P_4 and 30.0 g of S_8?

Answer available at the end of this section.

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Determining the Limiting Reactant and Theoretical Yield for a Reaction: Determining the Limiting Reactant and Theoretical Yield for a Reaction, YouTube(opens in new window) [youtu.be]

Limiting Reactants in Solutions

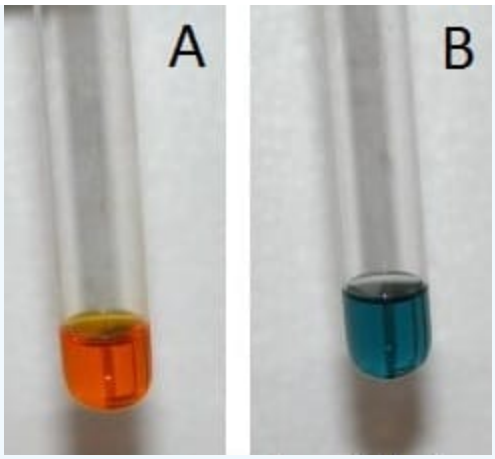
The concept of limiting reactants applies to reactions carried out in solution as well as to reactions involving pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example 3.7.2.

Example 3.7.2: Breathalyzer reaction

Because the consumption of alcoholic beverages adversely affects the performance of tasks that require skill and judgment, in most countries it is illegal to drive while under the influence of alcohol. In almost all US states, a blood alcohol level of 0.08% by volume is considered legally drunk. Higher levels cause acute intoxication (0.20%), unconsciousness (about 0.30%), and even death (about 0.50%). The Breathalyzer is a portable device that measures the ethanol concentration in a person's breath, which is directly proportional to the blood alcohol level. The reaction used in the Breathalyzer is the oxidation of ethanol by the dichromate ion:

$$3\,CH_3\ CH_2\ OH\,(aq) + 2\,\underset{yellow-orange}{Cr_2\ O_7{}^{2-}}(aq) + 16\,H^+\,(aq) \xrightarrow[H_2SO_4\,(aq)]{Ag^+} 3\,CH_3CO_2H\,(aq) + 4\,\underset{green}{Cr^{3+}}(aq) + 11\,H_2O\,(l)$$

When a measured volume (52.5 mL) of a suspect's breath is bubbled through a solution of excess potassium dichromate in dilute sulfuric acid, the ethanol is rapidly absorbed and oxidized to acetic acid by the dichromate ions. In the process, the chromium atoms in some of the $Cr_2O_7{}^{2-}$ ions are reduced from Cr^{6+} to Cr^{3+}. In the presence of Ag^+ ions that act as a catalyst, the reaction is complete in less than a minute. Because the $Cr_2O_7{}^{2-}$ ion (the reactant) is yellow-orange and the Cr^{3+} ion (the product) forms a green solution, the amount of ethanol in the person's breath (the limiting reactant) can be determined quite accurately by comparing the color of the final solution with the colors of standard solutions prepared with known amounts of ethanol.



A Breathalyzer reaction with a test tube before (a) and after (b) ethanol is added. When a measured volume of a suspect's breath is bubbled through the solution, the ethanol is oxidized to acetic acid, and the solution changes color from yellow-orange to green. The intensity of the green color indicates the amount of ethanol in the sample.

A typical Breathalyzer ampul contains 3.0 mL of a 0.25 mg/mL solution of $K_2Cr_2O_7$ in 50% H_2SO_4 as well as a fixed concentration of $AgNO_3$ (typically 0.25 mg/mL is used for this purpose). How many grams of ethanol must be present in 52.5 mL of a person's breath to convert all the Cr^{6+} to Cr^{3+}?

Given: volume and concentration of one reactant

Asked for: mass of other reactant needed for complete reaction

Strategy:

A. Calculate the number of moles of $Cr_2O_7^{2-}$ ion in 1 mL of the Breathalyzer solution by dividing the mass of $K_2Cr_2O_7$ by its molar mass.
B. Find the total number of moles of $Cr_2O_7^{2-}$ ion in the Breathalyzer ampul by multiplying the number of moles contained in 1 mL by the total volume of the Breathalyzer solution (3.0 mL).
C. Use the mole ratios from the balanced chemical equation to calculate the number of moles of C_2H_5OH needed to react completely with the number of moles of $Cr_2O_7^{2-}$ ions present. Then find the mass of C_2H_5OH needed by multiplying the number of moles of C_2H_5OH by its molar mass.

Solution:

A In any stoichiometry problem, the first step is always to calculate the number of moles of each reactant present. In this case, we are given the mass of $K_2Cr_2O_7$ in 1 mL of solution, which can be used to calculate the number of moles of $K_2Cr_2O_7$ contained in 1 mL:

$$\frac{moles\ K_2Cr_2O_7}{1\ mL} = \frac{(0.25\ \cancel{mg}\ K_2Cr_2O_7)}{mL}\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{294.18\ \cancel{g}\ K_2Cr_2O_7}\right) = 8.5 \times 10^{-7}\ moles$$

B Because 1 mol of $K_2Cr_2O_7$ produces 1 mol of $Cr_2O_7^{2-}$ when it dissolves, each milliliter of solution contains 8.5×10^{-7} mol of $Cr_2O_7^{2-}$. The total number of moles of $Cr_2O_7^{2-}$ in a 3.0 mL Breathalyzer ampul is thus

$$moles\ Cr_2O_7^{2-} = \left(\frac{8.5 \times 10^{-7}\ mol}{1\ \cancel{mL}}\right)(3.0\ \cancel{mL}) = 2.6 \times 10^{-6}\ mol\ Cr_2O_7^{2-}$$

C The balanced chemical equation tells us that 3 mol of C_2H_5OH is needed to consume 2 mol of $Cr_2O_7^{2-}$ ion, so the total number of moles of C_2H_5OH required for complete reaction is

$$moles\ of\ C_2H_5OH = (2.6 \times 10^{-6}\ \cancel{mol_{\ 2?}CrO^{2-}}) \left(\frac{3\ mol\ C_2H_5OH}{2\ \cancel{mol_{\ 2?}CrO^{2-}}} \right) = 3.9 \times 10^{-6}\ mol\ {}_2CH_5OH$$

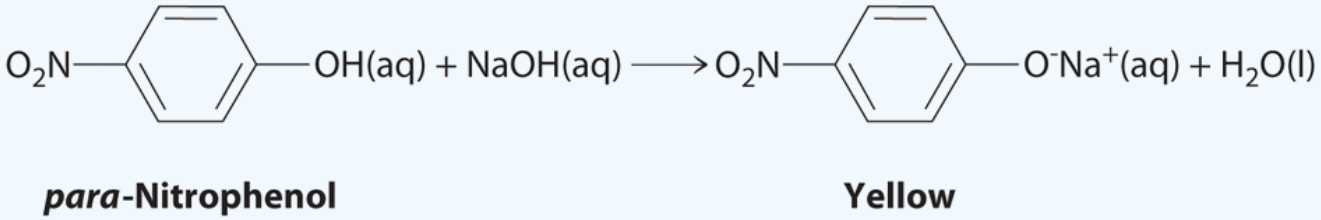
As indicated in the strategy, this number can be converted to the mass of C_2H_5OH using its molar mass:

$$mass\ {}_2CH_5OH = (3.9 \times 10^{-6}\ \cancel{mol\ {}_2CH_5OH}) \left(\frac{46.07\ g}{\cancel{mol\ {}_2CH_5OH}} \right) = 1.8 \times 10^{-4}\ g\ C_2H_5OH$$

Thus 1.8 × 10^{-4} g or 0.18 mg of C_2H_5OH must be present. Experimentally, it is found that this value corresponds to a blood alcohol level of 0.7%, which is usually fatal.

Exercise 3.7.2

The compound *para*-nitrophenol (molar mass = 139 g/mol) reacts with sodium hydroxide in aqueous solution to generate a yellow anion via the reaction



para-Nitrophenol **Yellow**

Chemical equation showing conversion of para-nitrophenol to its yellow-colored form with aqueous sodium hydroxide.

Because the amount of *para*-nitrophenol is easily estimated from the intensity of the yellow color that results when excess $NaOH$ is added, reactions that produce *para*-nitrophenol are commonly used to measure the activity of enzymes, the catalysts in biological systems. What volume of 0.105 M NaOH must be added to 50.0 mL of a solution containing 7.20 × 10^{-4} g of *para*-nitrophenol to ensure that formation of the yellow anion is complete?

Answer available at the end of this section.

In Examples 3.7.1 and 3.7.2, the identities of the limiting reactants are apparent: $[Au(CN)_2]^-$, $LaCl_3$, ethanol, and *para*-nitrophenol. When the limiting reactant is not apparent, it can be determined by comparing the molar amounts of the reactants with their coefficients in the balanced chemical equation. The only difference is that the volumes and concentrations of solutions of reactants, rather than the masses of reactants, are used to calculate the number of moles of reactants, as illustrated in Example 3.7.3.

Example 3.7.3

When aqueous solutions of silver nitrate and potassium dichromate are mixed, an exchange reaction occurs, and silver dichromate is obtained as a red solid. The overall chemical equation for the reaction is as follows:

$$2\,AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \rightarrow Ag_2Cr_2O_7\,(s) + 2\,KNO_3\,(aq)$$

What mass of $Ag_2Cr_2O_7$ is formed when 500 mL of 0.17 M $K_2Cr_2O_7$ are mixed with 250 mL of 0.57 M $AgNO_3$?

Given: balanced chemical equation and volume and concentration of each reactant

Asked for: mass of product

Strategy:

A. Calculate the number of moles of each reactant by multiplying the volume of each solution by its molarity.
B. Determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation.
C. Use mole ratios to calculate the number of moles of product that can be formed from the limiting reactant. Multiply the number of moles of the product by its molar mass to obtain the corresponding mass of product.

Solution:

A The balanced chemical equation tells us that 2 mol of $AgNO_3$(aq) reacts with 1 mol of $K_2Cr_2O_7$(aq) to form 1 mol of $Ag_2Cr_2O_7$(s) (Figure 8.3.2). The first step is to calculate the number of moles of each reactant in the specified volumes:

$$moles\ K_2Cr_2O_7 = 500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.17\ mol\ K_2Cr_2O_7}{1\ \cancel{L}}\right) = 0.085\ mol\ K_2Cr_2O_7$$

$$moles\ AgNO_3 = 250\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.57\ mol\ AgNO_3}{1\ \cancel{L}}\right) = 0.14\ mol\ AgNO_3$$

B Now determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

$$\mathrm{K_2Cr_2O_7}: \frac{0.085\ mol}{1\ mol} = 0.085$$

$$\mathrm{AgNO_3}: \frac{0.14\ mol}{2\ mol} = 0.070$$

Because 0.070 < 0.085, we know that $\mathrm{AgNO_3}$ is the *limiting reactant*.

C Each mole of $\mathrm{Ag_2Cr_2O_7}$ formed requires 2 mol of the limiting reactant ($\mathrm{AgNO_3}$), so we can obtain only 0.14/2 = 0.070 mol of $\mathrm{Ag_2Cr_2O_7}$. Finally, convert the number of moles of $\mathrm{Ag_2Cr_2O_7}$ to the corresponding mass:

$$mass\ of\ Ag_2Cr_2O_7 = 0.070\ \cancel{mol}\left(\frac{431.72\ g}{1\ \cancel{mol}}\right) = 30\ g\ Ag_2Cr_2O_7$$

The Ag^+ and $Cr_2O_7^{2-}$ ions form a red precipitate of solid $\mathrm{Ag_2Cr_2O_7}$, while the $\mathrm{K^+}$ and $\mathrm{NO_3^-}$ ions remain in solution. (Water molecules are omitted from molecular views of the solutions for clarity.)

Exercise 3.7.3

Aqueous solutions of sodium bicarbonate and sulfuric acid react to produce carbon dioxide according to the following equation:

$$\mathrm{2\,NaHCO_3\,(aq) + H_2SO_4\,(aq) \rightarrow 2\,CO_2\,(g) + Na_2SO_4\,(aq) + 2\,H_2O\,(l)}$$

If 13.0 mL of 3.0 M H_2SO_4 are added to 732 mL of 0.112 M $NaHCO_3$, what mass of CO_2 is produced?

Answer available at the end of this section.

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Limiting Reactant Problems Using Molarities: Limiting Reactant Problems Using Molarities, YouTube(opens in new window)
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Theoretical Yields

When reactants are not present in stoichiometric quantities, the limiting reactant determines the maximum amount of product that can be formed from the reactants. The amount of product calculated in this way is the theoretical yield, the amount obtained if the reaction occurred perfectly and the purification method were 100% efficient.

In reality, less product is always obtained than is theoretically possible because of mechanical losses (such as spilling), separation procedures that are not 100% efficient, competing reactions that form undesired products, and reactions that simply do not run to completion, resulting in a mixture of products and reactants; this last possibility is a common occurrence. Therefore, the actual yield, the measured mass of products obtained from a reaction, is almost always less than the theoretical yield (often much less). The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, multiplied by 100 to give a percentage:

$$\text{percent yield} = \frac{\text{actual yield } (g)}{\text{theoretical yield } (g)} \times 100\% \tag{3.7.5}$$

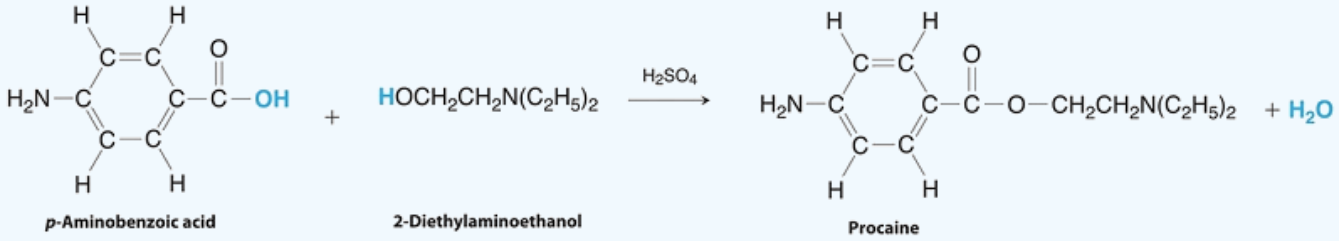
The method used to calculate the percent yield of a reaction is illustrated in Example 3.7.4.

Example 3.7.4: Novocain

Procaine is a key component of Novocain, an injectable local anesthetic used in dental work and minor surgery. Procaine can be prepared in the presence of H2SO4 (indicated above the arrow) by the reaction

$$\underset{\text{p-amino benzoic acid}}{C_7H_7NO_2} + \underset{\text{2-diethylaminoethanol}}{C_6H_{15}NO} \xrightarrow{H_2SO_4} \underset{\text{procaine}}{C_{13}H_{20}N_2O_2} + H_2O$$

If this reaction were carried out with 10.0 g of p-aminobenzoic acid and 10.0 g of 2-diethylaminoethanol, and 15.7 g of procaine were isolated, what is the percent yield?



The preparation of procaine. A reaction of p-aminobenzoic acid with 2-diethylaminoethanol yields procaine and water.

Given: masses of reactants and product

Asked for: percent yield

Strategy:

A. Write the balanced chemical equation.
B. Convert from mass of reactants and product to moles using molar masses and then use mole ratios to determine which is the limiting reactant. Based on the number of moles of the limiting reactant, use mole ratios to determine the theoretical yield.
C. Calculate the percent yield by dividing the actual yield by the theoretical yield and multiplying by 100.

Solution:

A From the formulas given for the reactants and the products, we see that the chemical equation is balanced as written. According to the equation, 1 mol of each reactant combines to give 1 mol of product plus 1 mol of water.

B To determine which reactant is limiting, we need to know their molar masses, which are calculated from their structural formulas: p-aminobenzoic acid ($C_7H_7NO_2$), 137.14 g/mol; 2-diethylaminoethanol ($C_6H_{15}NO$), 117.19 g/mol. Thus the reaction used the following numbers of moles of reactants:

$$mol \text{ p-aminobenzoic acid} = 10.0\,g \times \frac{1\,mol}{137.14\,g} = 0.0729\,mol \text{ p-aminbenzoic acid}$$

$$mol \text{ 2-diethylaminoethanol} = 10.0\,g \times \frac{1\,mol}{117.19\,g} = 0.0853\,mol \text{ 2-diethylaminoethanol}$$

The reaction requires a 1:1 mole ratio of the two reactants, so p-aminobenzoic acid is the limiting reactant. Based on the coefficients in the balanced chemical equation, 1 mol of p-aminobenzoic acid yields 1 mol of procaine. We can therefore obtain only a maximum of 0.0729 mol of procaine. To calculate the corresponding mass of procaine, we use its structural formula (C13H20N2O2) to calculate its molar mass, which is 236.31 g/mol.

$$\text{theoretical yield of procaine} = 0.0729\,mol \times \frac{236.31\,g}{1\,mol} = 17.2\,g$$

C The actual yield was only 15.7 g of procaine, so the percent yield (via Equation 3.7.5) is

$$\text{percent yield} = \frac{15.7\,g}{17.2\,g} \times 100 = 91.3\%$$

(If the product were pure and dry, this yield would indicate very good lab technique!)

Exercise 3.7.4: Extraction of Lead

Lead was one of the earliest metals to be isolated in pure form. It occurs as concentrated deposits of a distinctive ore called galena (PbS), which is easily converted to lead oxide (PbO) in 100% yield by roasting in air via the following reaction:

$$2\,PbS\,(s) + 3\,O_2 \rightarrow 2\,PbO\,(s) + 2\,SO_2\,(g)$$

The resulting PbO is then converted to the pure metal by reaction with charcoal. Because lead has such a low melting point (327°C), it runs out of the ore-charcoal mixture as a liquid that is easily collected. The reaction for the conversion of lead oxide to pure lead is as follows:

$$PbO\,(s) + C\,(s) \rightarrow Pb\,(l) + CO\,(g)$$

If 93.3 kg of PbO is heated with excess charcoal and 77.3 kg of pure lead is obtained, what is the percent yield?



Electrolytically refined pure (99.989 %) superficially oxidized lead nodules and a high purity (99.989 %) $1\ cm^3$ lead cube for comparison. Figure used with permission from Wikipedia.

Answer available at the end of this section.

Percent yield can range from 0% to 100%. In the laboratory, a student will occasionally obtain a yield that appears to be greater than 100%. This usually happens when the product is impure or is wet with a solvent such as water. If this is not the case, then the student must have made an error in weighing either the reactants or the products. The law of conservation of mass applies even to undergraduate chemistry laboratory experiments. A 100% yield means that everything worked perfectly, and the chemist obtained all the product that could have been produced. Anyone who has tried to do something as simple as fill a salt shaker or add oil to a car's engine without spilling knows the unlikelihood of a 100% yield. At the other extreme, a yield of 0% means that no product was obtained. A percent yield of 80%–90% is usually considered good to excellent; a yield of 50% is only fair. In part because of the problems and costs of waste disposal, industrial production facilities face considerable pressures to optimize the yields of products and make them as close to 100% as possible.

Summary

The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained. The stoichiometry of a reaction describes the relative amounts of reactants and products in a balanced chemical equation. A stoichiometric quantity of a reactant is the amount necessary to react completely with the other reactant(s). If a quantity of a reactant remains unconsumed after complete reaction has occurred, it is in excess. The reactant that is consumed first and limits the amount of product(s) that can be obtained is the limiting reactant. To identify the limiting reactant, calculate the number of moles of each reactant present and compare this ratio to the mole ratio of the reactants in the balanced chemical equation. The maximum amount of product(s) that can be obtained in a reaction from a given amount of reactant(s) is the theoretical yield of the reaction. The actual yield is the amount of product(s) actually obtained in the reaction; it cannot exceed the theoretical yield. The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, expressed as a percentage.

Answers

Exercise 3.7.1

35.9 g

Exercise 3.7.2

4.93×10^{-5} L or 49.3 µL

Exercise 3.7.3

3.4 g

Exercise 3.7.4**: Extraction of Lead**

89.2%

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3.E: Stoichiometry (Exercises)

3.1: Chemical Equations

Conceptual Problems

1. How does a balanced chemical equation agree with the law of definite proportions?
2. What is the difference between S_8 and 8S? Use this example to explain why subscripts in a formula must not be changed.
3. What factors determine whether a chemical equation is balanced?
4. What information can be obtained from a balanced chemical equation? Does a balanced chemical equation give information about the rate of a reaction?

Numerical Problems

1. Balance each chemical equation.

   a. $KI(aq) + Br_2(l) \rightarrow KBr(aq) + I_2(s)$

   b. $MnO_2(s) + HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + H_2O(l)$

   c. $Na_2O(s) + H_2O(l) \rightarrow NaOH(aq)$

   d. $Cu(s) + AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + Ag(s)$

   e. $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

   f. $S_2Cl_2(l) + NH_3(l) \rightarrow S_4N_4(s) + S_8(s) + NH_4Cl(s)$

2. Balance each chemical equation.

   a. $Be(s) + O_2(g) \rightarrow BeO(s)$

   b. $N_2O_3(g) + H_2O(l) \rightarrow HNO_2(aq)$

   c. $Na(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$

   d. $CaO(s) + HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l)$

   e. $CH_3NH_2(g) + O_2(g) \rightarrow H_2O(g) + CO_2(g) + N_2(g)$

   f. $Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$

3. Balance each chemical equation.

   a. $N_2O_5(g) \rightarrow NO_2(g) + O_2(g)$

   b. $NaNO_3(s) \rightarrow NaNO_2(s) + O_2(g)$

   c. $Al(s) + NH_4NO_3(s) \rightarrow N_2(g) + H_2O(l) + Al_2O_3(s)$

   d. $C_3H_5N_3O_9(l) \rightarrow CO_2(g) + N_2(g) + H_2O(g) + O_2(g)$

   e. reaction of butane with excess oxygen

f. $IO_2F(s) + BrF_3(l) \rightarrow IF_5(l) + Br_2(l) + O_2(g)$

4. Balance each chemical equation.

a. $H_2S(g) + O_2(g) \rightarrow H_2O(l) + S_8(s)$

b. $KCl(aq) + HNO_3(aq) + O_2(g) \rightarrow KNO_3(aq) + Cl_2(g) + H_2O(l)$

c. $NH_3(g) + O_2(g) \rightarrow NO(g) + H_2O(g)$

d. $CH_4(g) + O_2(g) \rightarrow CO(g) + H_2(g)$

e. $NaF(aq) + Th(NO_3)_4(aq) \rightarrow NaNO_3(aq) + ThF_4(s)$

f. $Ca_5(PO_4)_3F(s) + H_2SO_4(aq) + H_2O(l) \rightarrow H_3PO_4(aq) + CaSO_4 \bullet 2H_2O(s) + HF(aq)$

5. Balance each chemical equation.

a. $NaCl(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + HCl(g)$

b. $K(s) + H_2O(l) \rightarrow KOH(aq) + H_2(g)$

c. reaction of octane with excess oxygen

d. $S_8(s) + Cl_2(g) \rightarrow S_2Cl_2(l)$

e. $CH_3OH(l) + I_2(s) + P_4(s) \rightarrow CH_3I(l) + H_3PO_4(aq) + H_2O(l)$

f. $(CH_3)_3Al(s) + H_2O(l) \rightarrow CH_4(g) + Al(OH)_3(s)$

6. Write a balanced chemical equation for each reaction.

a. Aluminum reacts with bromine.

b. Sodium reacts with chlorine.

c. Aluminum hydroxide and acetic acid react to produce aluminum acetate and water.

d. Ammonia and oxygen react to produce nitrogen monoxide and water.

e. Nitrogen and hydrogen react at elevated temperature and pressure to produce ammonia.

f. An aqueous solution of barium chloride reacts with a solution of sodium sulfate.

7. Write a balanced chemical equation for each reaction.

a. Magnesium burns in oxygen.

b. Carbon dioxide and sodium oxide react to produce sodium carbonate.

c. Aluminum reacts with hydrochloric acid.

d. An aqueous solution of silver nitrate reacts with a solution of potassium chloride.

e. Methane burns in oxygen.

f. Sodium nitrate and sulfuric acid react to produce sodium sulfate and nitric acid.

3.2: Some Simple Patterns of Chemical Reactivity

3.3: Formula Masses

Conceptual Problems

1. What is the relationship between an empirical formula and a molecular formula
2. Construct a flowchart showing how you would determine the empirical formula of a compound from its percent composition.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 3.7 "Essential Skills 2") before proceeding to the Numerical Problems.

a. What is the formula mass of each species?

a. ammonium chloride

b. sodium cyanide

c. magnesium hydroxide

d. calcium phosphate

e. lithium carbonate

f. hydrogen sulfite ion

b. What is the molecular or formula mass of each compound?

a. potassium permanganate

b. sodium sulfate

c. hydrogen cyanide

d. potassium thiocyanate

e. ammonium oxalate

f. lithium acetate

1. What is the mass percentage of water in each hydrate?

a. $H_3AsO_4 \cdot 5H_2O$

b. $NH_4NiCl_3 \cdot 6H_2O$

c. $Al(NO_3)_3 \cdot 9H_2O$

2. What is the mass percentage of water in each hydrate?

a. $CaSO_4 \cdot 2H_2O$

b. $Fe(NO_3)_3 \cdot 9H_2O$

c. $(NH_4)_3ZrOH(CO_3)_3 \cdot 2H_2O$

3. Which of the following has the greatest mass percentage of oxygen—$KMnO_4$, $K_2Cr_2O_7$, or Fe_2O_3?

4. Which of the following has the greatest mass percentage of oxygen—$ThOCl_2$, $MgCO_3$, or NO_2Cl?

5. Calculate the percent composition of the element shown in bold in each compound.

a. Sb**Br**$_3$

b. **As**$_2$I$_4$

c. Al**P**O$_4$

d. **C**$_6$H$_{10}$O

6. Calculate the percent composition of the element shown in bold in each compound.

a. H**Br**O$_3$

b **Cs**ReO$_4$

c. **C**$_3$H$_8$O

d. Fe**S**O$_4$

7. A sample of a chromium compound has a molar mass of 151.99 g/mol. Elemental analysis of the compound shows that it contains 68.43% chromium and 31.57% oxygen. What is the identity of the compound?

8. The percentages of iron and oxygen in the three most common binary compounds of iron and oxygen are given in the following table. Write the empirical formulas of these three compounds.

Compound	% Iron	% Oxygen	Empirical Formula
1	69.9	30.1	
2	77.7	22.3	
3	72.4	27.6	

9. What is the mass percentage of water in each hydrate?

a. LiCl·H$_2$O

b. MgSO$_4$·7H$_2$O

c. Sr(NO$_3$)$_2$·4H$_2$O

10. What is the mass percentage of water in each hydrate?

a. CaHPO$_4$·2H$_2$O

b. FeCl$_2$·4H$_2$O

c. Mg(NO$_3$)$_2$·4H$_2$O

11. Two hydrates were weighed, heated to drive off the waters of hydration, and then cooled. The residues were then reweighed. Based on the following results, what are the formulas of the hydrates?

Compound	Initial Mass (g)	Mass after Cooling (g)
NiSO$_4$·xH$_2$O	2.08	1.22
CoCl$_2$·xH$_2$O	1.62	0.88

12. Which contains the greatest mass percentage of sulfur—FeS_2, $Na_2S_2O_4$, or Na_2S?

13. Given equal masses of each, which contains the greatest mass percentage of sulfur—$NaHSO_4$ or K_2SO_4?

14. Calculate the mass percentage of oxygen in each polyatomic ion.

a. bicarbonate

b. chromate

c. acetate

d. sulfite

15. Calculate the mass percentage of oxygen in each polyatomic ion.

a. oxalate

b. nitrite

c. dihydrogen phosphate

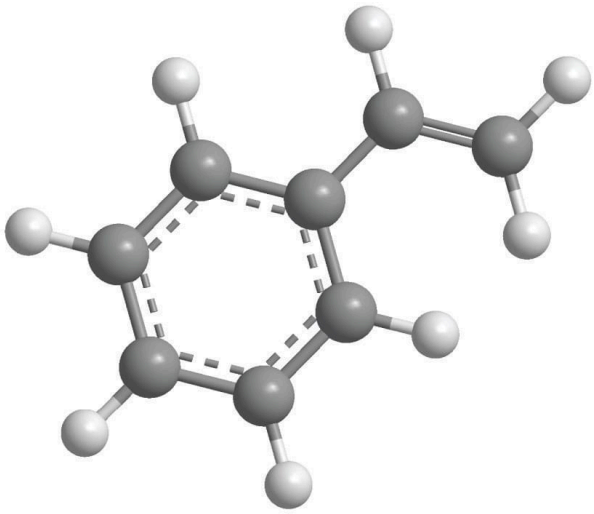
d. thiocyanate

16. The empirical formula of garnet, a gemstone, is $Fe_3Al_2Si_3O_{12}$. An analysis of a sample of garnet gave a value of 13.8% for the mass percentage of silicon. Is this consistent with the empirical formula?

17. A compound has the empirical formula C_2H_4O, and its formula mass is 88 g. What is its molecular formula?

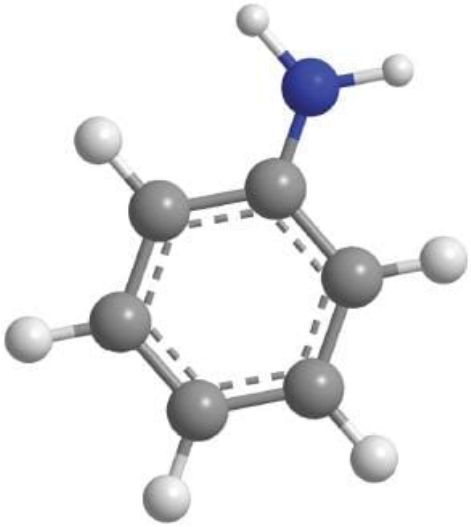
18. Mirex is an insecticide that contains 22.01% carbon and 77.99% chlorine. It has a molecular mass of 545.59 g. What is its empirical formula? What is its molecular formula?

19. How many moles of CO_2 and H_2O will be produced by combustion analysis of 0.010 mol of styrene?



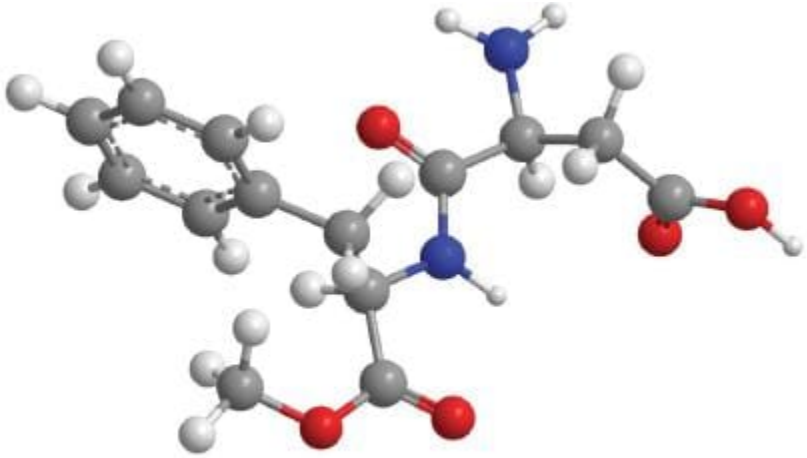
Styrene

20. How many moles of CO_2, H_2O, and N_2 will be produced by combustion analysis of 0.0080 mol of aniline?



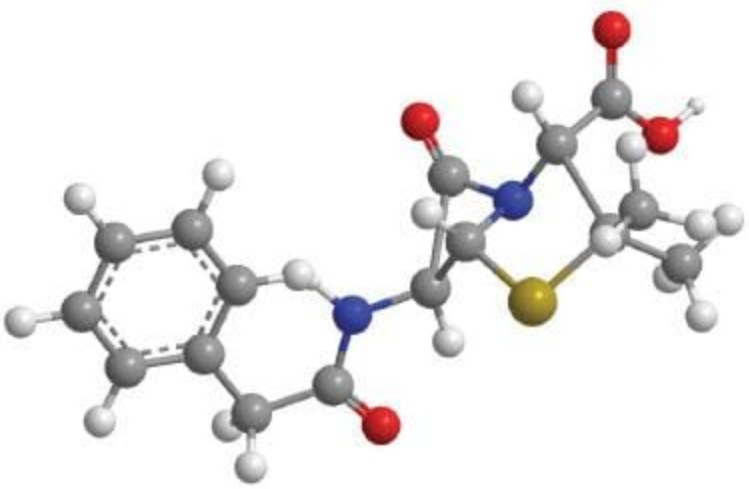
Aniline

21. How many moles of CO_2, H_2O, and N_2 will be produced by combustion analysis of 0.0074 mol of aspartame?



Aspartame

22. How many moles of CO_2, H_2O, N_2, and SO_2 will be produced by combustion analysis of 0.0060 mol of penicillin G?



Penicillin G

23. Combustion of a 34.8 mg sample of benzaldehyde, which contains only carbon, hydrogen, and oxygen, produced 101 mg of CO_2 and 17.7 mg of H_2O.

a. What was the mass of carbon and hydrogen in the sample?

b. Assuming that the original sample contained only carbon, hydrogen, and oxygen, what was the mass of oxygen in the sample?

c. What was the mass percentage of oxygen in the sample?

d. What is the empirical formula of benzaldehyde?

e. The molar mass of benzaldehyde is 106.12 g/mol. What is its molecular formula?

24. Salicylic acid is used to make aspirin. It contains only carbon, oxygen, and hydrogen. Combustion of a 43.5 mg sample of this compound produced 97.1 mg of CO_2 and 17.0 mg of H_2O.

a. What is the mass of oxygen in the sample?

b. What is the mass percentage of oxygen in the sample?

c. What is the empirical formula of salicylic acid?

d. The molar mass of salicylic acid is 138.12 g/mol. What is its molecular formula?

25. Given equal masses of the following acids, which contains the greatest amount of hydrogen that can dissociate to form H^+—nitric acid, hydroiodic acid, hydrocyanic acid, or chloric acid?

26. Calculate the formula mass or the molecular mass of each compound.

a. heptanoic acid (a seven-carbon carboxylic acid)

b. 2-propanol (a three-carbon alcohol)

c. $KMnO_4$

d. tetraethyllead

e. sulfurous acid

f. ethylbenzene (an eight-carbon aromatic hydrocarbon)

27. Calculate the formula mass or the molecular mass of each compound.

a. $MoCl_5$

b. B_2O_3

c. bromobenzene

d. cyclohexene

e. phosphoric acid

f. ethylamine

28. Given equal masses of butane, cyclobutane, and propene, which contains the greatest mass of carbon?

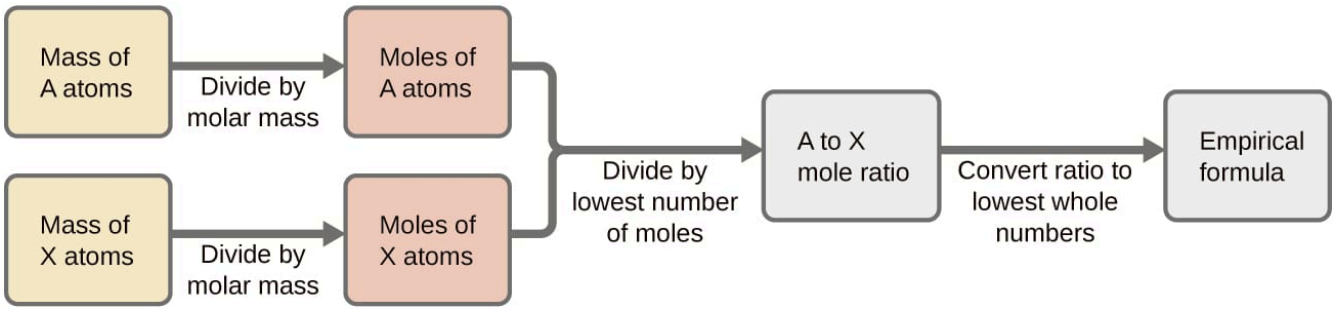
29. Given equal masses of urea [$(NH_2)_2CO$] and ammonium sulfate, which contains the most nitrogen for use as a fertilizer?

Conceptual Answers

1) What is the relationship between an empirical formula and a molecular formula

- An empirical formula refers to the simplest ratio of elements that is obtained from a chemical formula while a molecular formula is calculated to show the actual formula of a molecular compound.

2) Construct a flowchart showing how you would determine the empirical formula of a compound from its percent composition.



Numerical Answers

a. What is the formula mass of each species?

a. 53.49146 amu

b. 49.0072 amu

c. 58.3197 amu

d. 310.177 amu

e. 73.891 amu

f. 81.07 amu

b. What is the molecular or formula mass of each compound?

a.158.034 amu

b. 142.04 amu

c. 27.0253 amu

d. 97.181 amu

e. 124.1 amu

f. 65.99 amu

1. To two decimal places, the percentages are:

a. 5.97%

b. 37.12%

c. 43.22%

2. To two decimal places, the percentages of water are:

a. 20.93%

b. 40.13%

c. 9.52%

3. % oxygen: $KMnO_4$, 40.50%; $K_2Cr_2O_7$, 38.07%; Fe_2O_3, 30.06%

4. % oxygen: ThOCl2, 5.02%; MgCO3, 56.93%; NO2Cl, 39.28%

5. To two decimal places, the percentages are:

a. 66.32% Br

b. 22.79% As

c. 25.40% P

d. 73.43% C

6.

a. 61.98% Br

b. 34.69% Cs

c. 59.96% C

d. 21.11% S

7. Cr_2O_3.

8. Empirical Formulas

1. Fe_2O_3
2. Fe_4O_4
3. Fe_6O_8

9. To two decimal places, the percentages are:

a. 29.82%

b. 51.16%

c. 25.40%

10. What is the mass percentage of water in each hydrate?

a. 20.94%

b. 36.25%

c. 32.70%

11. $NiSO_4 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$

12. FeS_2

13. $NaHSO_4$

14. Calculate the mass percentage of oxygen in each polyatomic ion.

a. 78.66%

b. 55.17%

c. 54.19%

d. 59.95%

15.

a. 72.71%

b. 69.55%

c. 65.99%

d. 0%

16. The empirical formula of garnet, a gemstone, is $Fe_3Al_2Si_3O_{12}$. An analysis of a sample of garnet gave a value of 13.8% for the mass percentage of silicon. Is this consistent with the empirical formula?

No, the calculated mass percentage of silicon in garnet is 16.93%

17. $C_4H_8O_2$

18.

Empirical Formula: $C_{10}Cl_{12}$

Molecular Formula: $C_{10}Cl_{12}$

19. How many moles of CO_2 and H_2O will be produced by combustion analysis of 0.010 mol of styrene?

Moles of CO2: 0.08 mol CO_2

Moles of H2O: 0.04 mol H_2O

20. How many moles of CO_2, H_2O, and N_2 will be produced by combustion analysis of 0.0080 mol of aniline?

Mole of CO2: 0.048 mol CO_2

Mole of H2O: 0.028 mol H_2O

Mole of N2: 0.004 mol N_2

21. How many moles of CO_2, H_2O, and N_2 will be produced by combustion analysis of 0.0074 mol of aspartame?

Mole of CO2: 0.104 mol CO_2

Mole of H2O: 0.666 mol H_2O

Mole of N2: 0.0074 mol N_2

22. How many moles of CO_2, H_2O, N_2, and SO_2 will be produced by combustion analysis of 0.0060 mol of penicillin G?

Mole of CO2: 0.096 mol CO_2

Mole of H2O: 0.054 mol H_2O

Mole of N2: 0.060 mol N_2

Mole of SO2: 0.060 mol SO_2

23.

a. 27.6 mg C and 1.98 mg H

b. 5.2 mg O

c. 15%

d. C_7H_6O

e. C_7H_6O

24. Salicylic acid is used to make aspirin. It contains only carbon, oxygen, and hydrogen. Combustion of a 43.5 mg sample of this compound produced 97.1 mg of CO_2 and 17.0 mg of H_2O.

a. What is the mass of oxygen in the sample?

70.4mg

b. What is the mass percentage of oxygen in the sample?

61.70%

c. What is the empirical formula of salicylic acid?

$C_7H_6O_3$

d. The molar mass of salicylic acid is 138.12 g/mol. What is its molecular formula?

$C_7H_6O_3$

25. hydrocyanic acid, HCN

26. Calculate the formula mass or the molecular mass of each compound.

a. 130.1849 amu

b. 60.1 amu

c. 158.034 amu

d. 323.4 amu

e. 82.07 amu

f. 106.17 amu

27. To two decimal places, the values are:

a. 273.23 amu

b. 69.62 amu

c. 157.01 amu

d. 82.14 amu

e. 98.00 amu

f. 45.08 amu

28. Cyclobutene

29. Urea

3.4: Avogadro's Number and the Mole

Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 2 before proceeding to the Conceptual Problems.

1. Describe the relationship between an atomic mass unit and a gram.
2. Is it correct to say that ethanol has a formula mass of 46? Why or why not?
3. If 2 mol of sodium reacts completely with 1 mol of chlorine to produce sodium chloride, does this mean that 2 g of sodium reacts completely with 1 g of chlorine to give the same product? Explain your answer.
4. Construct a flowchart to show how you would calculate the number of moles of silicon in a 37.0 g sample of orthoclase ($KAlSi_3O_8$), a mineral used in the manufacture of porcelain.
5. Construct a flowchart to show how you would calculate the number of moles of nitrogen in a 22.4 g sample of nitroglycerin that contains 18.5% nitrogen by mass.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 2 before proceeding to the Numerical Problems.

1. Derive an expression that relates the number of molecules in a sample of a substance to its mass and molecular mass.

2. Calculate the molecular mass or formula mass of each compound.

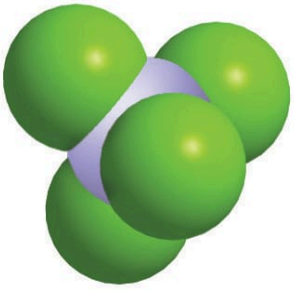
a. KCl (potassium chloride)
b. NaCN (sodium cyanide)
c. H_2S (hydrogen sulfide)
d. NaN_3 (sodium azide)
e. H_2CO_3 (carbonic acid)
f. K_2O (potassium oxide)
g. $Al(NO_3)_3$ (aluminum nitrate)
h. $Cu(ClO_4)_2$ [copper(II) perchlorate]

3. Calculate the molecular mass or formula mass of each compound.

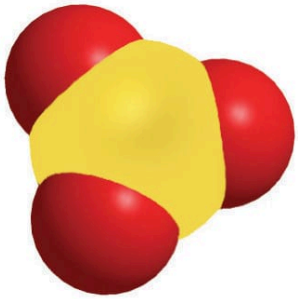
a. V_2O_4 (vanadium(IV) oxide)
b. $CaSiO_3$ (calcium silicate)
c. BiOCl (bismuth oxychloride)
d. CH_3COOH (acetic acid)
e. Ag_2SO_4 (silver sulfate)
f. Na_2CO_3 (sodium carbonate)
g. $(CH_3)_2CHOH$ (isopropyl alcohol)

4. Calculate the molar mass of each compound.

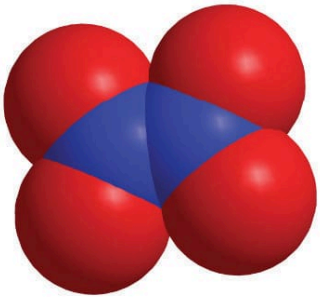
a.



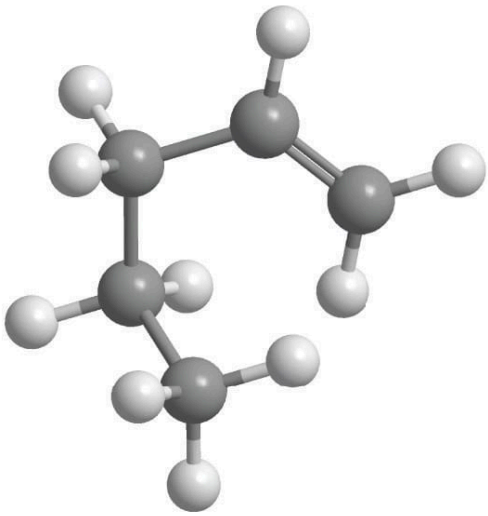
b.



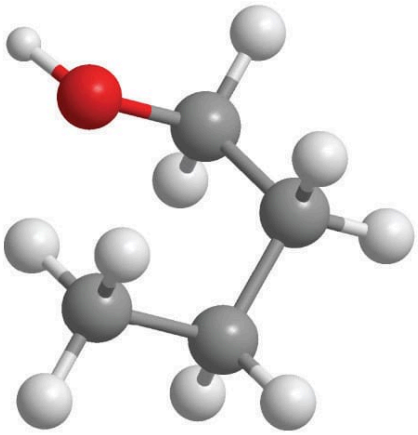
c.



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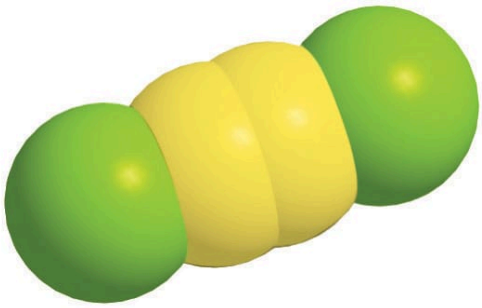


5. Calculate the molar mass of each compound.

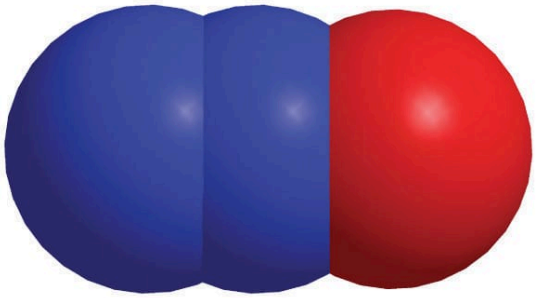
a.



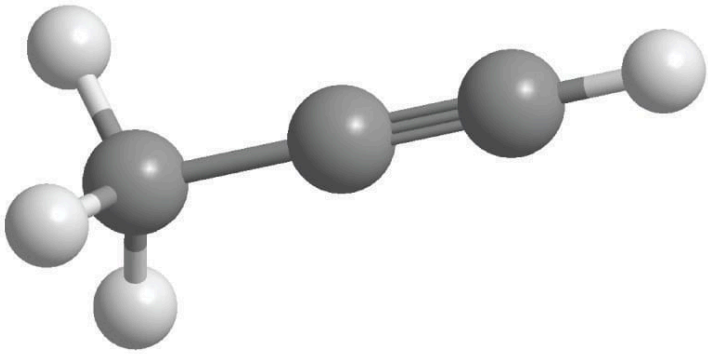
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c.

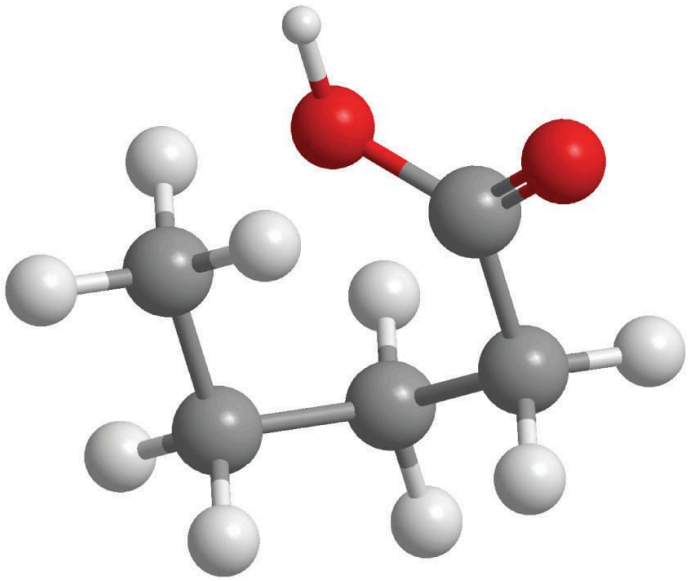


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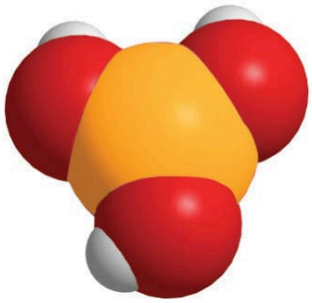


6. For each compound, write the condensed formula, name the compound, and give its molar mass.

a.

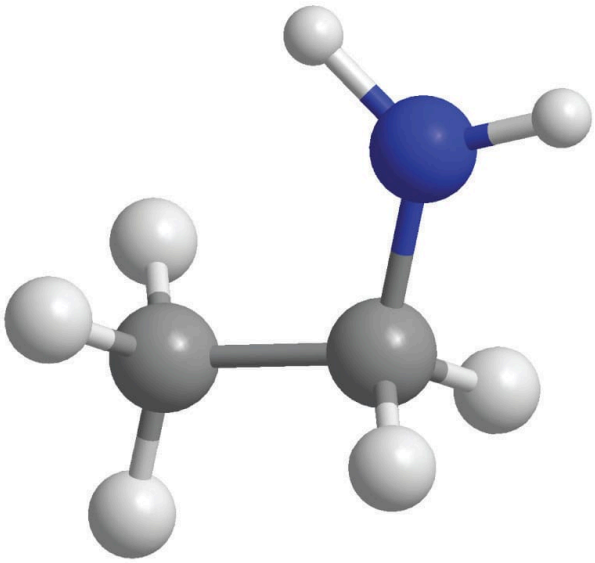


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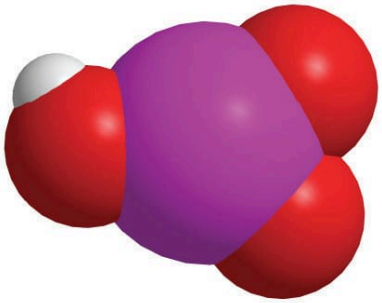


7. For each compound, write the condensed formula, name the compound, and give its molar mass.

a.



b.



8. Calculate the number of moles in 5.00×10^2 g of each substance. How many molecules or formula units are present in each sample?

a. CaO (lime)

b. $CaCO_3$(chalk)

c. $C_{12}H_{22}O_{11}$ [sucrose (cane sugar)]

d. NaOCl (bleach)

e. CO_2 (dry ice)

9. Calculate the mass in grams of each sample.

a. 0.520 mol of N_2O_4

b. 1.63 mol of $C_6H_4Br_2$

c. 4.62 mol of $(NH_4)_2SO_3$

10. Give the number of molecules or formula units in each sample.

a. 1.30×10^{-2} mol of SCl_2

b. 1.03 mol of N_2O_5

c. 0.265 mol of $Ag_2Cr_2O_7$

11. Give the number of moles in each sample.

a. 9.58×10^{26} molecules of Cl_2

b. 3.62×10^{27} formula units of KCl

c. 6.94×10^{28} formula units of $Fe(OH)_2$

12. Solutions of iodine are used as antiseptics and disinfectants. How many iodine atoms correspond to 11.0 g of molecular iodine (I_2)?

13. What is the total number of atoms in each sample?

a. 0.431 mol of Li

b. 2.783 mol of methanol (CH_3OH)

c. 0.0361 mol of $CoCO_3$

d. 1.0002 mol of $SeBr_2O$

14. What is the total number of atoms in each sample?

a. 0.980 mol of Na

b. 2.35 mol of O_2

c. 1.83 mol of Ag_2S

d. 1.23 mol of propane (C_3H_8)

15. What is the total number of atoms in each sample?

a. 2.48 g of HBr

b. 4.77 g of CS_2

c. 1.89 g of NaOH

d. 1.46 g of SrC_2O_4

16. Decide whether each statement is true or false and explain your reasoning.

a. There are more molecules in 0.5 mol of Cl_2than in 0.5 mol of H_2.
b. One mole of H_2 has 6.022×10^{23} hydrogen atoms.
c. The molecular mass of H_2O is 18.0 amu.
d. The formula mass of benzene is 78 amu.

17. Complete the following table.

Substance	Mass (g)	Number of Moles	Number of Molecules or Formula Units	Number of Atoms or Ions
$MgCl_2$	37.62	a.	b.	c.
$AgNO_3$	d.	2.84	e.	f.
BH_4Cl	g.	h.	8.93×10^{25}	i.
K_2S	j	k.	l.	7.69×10^{26}
H_2SO_4	m.	1.29	n.	o.
C_6H_{14}	11.84	p.	q.	r.
$HClO_3$	s.	t.	2.45×10^{26}	u.

18. Give the formula mass or the molecular mass of each substance.

a. $PbClF$
b. $Cu_2P_2O_7$
c. $BiONO_3$
d. Tl_2SeO_4

19. Give the formula mass or the molecular mass of each substance.

a. $MoCl_5$
b. B_2O_3
c. UO_2CO_3
d. $NH_4UO_2AsO_4$

Conceptual Answers

1. While both are units of mass, a gram is Avogadro's number of atomic mass units so you would multiply the number of amu by 6.022x10^23 to find total number of grams
2. The correct way to state formula mass of ethanol is to show the units of mass which is amu.
3. No because moles and weight operate on different set of standards meaning that they're not equal to each other. This means that moles of different compounds contain different weights. For example, 2 moles of Na = 2 x 22.989 g = 45.98g while 1 mole of Cl = 1 x 35.453 g = 35.453 g Cl. This makes the sodium react completely with chlorine. 2g of sodium would react with = (35.453/45.978) x 2 = 1.542 g Cl
4. Construct a flowchart to show how you would calculate the number of moles of silicon in a 37.0 g sample of orthoclase ($KAlSi_3O_8$), a mineral used in the manufacture of porcelain
    1. .

$$\frac{given\ mass}{molar\ mass\ of\ KAlSi3O8} x \frac{(3\ moles\ of\ Si)}{(1\ mole\ of\ KAlSi3O8)} = \frac{37\ mol}{278\ mol} x \frac{(3\ moles\ of\ Si)}{(1\ mole\ of\ KAlSi3O8)} = 0.4\ moles$$

5. Construct a flowchart to show how you would calculate the number of moles of nitrogen in a 22.4 g sample of nitroglycerin that contains 18.5% nitrogen by mass.

$$\frac{given\ mass\ of\ nitroglycerin}{molar\ mass\ of\ nitroglcerin} x \frac{(3\ moles\ of\ Si)}{(1\ mole\ of\ KAlSi3O8)} = \frac{22.4\ g}{227.0\ g/mol} = 0.099\ mole \rightarrow \frac{4.14\ (mass\ of\ nitrogen)}{14\ (molar\ atomic\ mass\ of\ nitrogen)} = 0.296\ moles$$

    1.
6. The information required to determine the mass of the solute would be the molarity of the solution because once that is achieved, volume of the solution and molar mass of the solute can be used to calculate the total mass. A derivatization that achieves this goes as: Molarity = moles of solute / volume of solution in liter -> Moles = molarity x volume in liter -> Mass= moles x molar mass.

Numerical Answers

1. Derive an expression that relates the number of molecules in a sample of a substance to its mass and molecular mass.

$$1\ mole = 6.022x10^{23} mol = NA\ (Avogadro's\ Number)$$

$$mole = \frac{mass}{molecular\ mass}$$

$$Number\ of\ molecules = moles\ x\ NA \rightarrow \frac{mass}{molecular\ mass} xNA$$

2. Calculate the molecular mass or formula mass of each compound.

    a. 74.55 amu
    b. 49.01 amu
    c. 34.08 amu
    d. 65.01 amu
    e. 62.02 amu
    f. 94.20 amu
    g. 213.00 amu
    h. 262.45 amu

3. Calculate the molecular mass or formula mass of each compound.

    a. 165.88 amu
    b. 116.16 amu
    c. 260.43 amu
    d. 60.05 amu

e. 311.80 amu
f. 105.99 amu
g. 60.10 amu

4. Calculate the molar mass of each compound.

a. 153.82 g/mol

b. 80.06 g/mol

c. 92.01 g/mol

d. 70.13 g/mol

e. 74.12 g/mol

5. Calculate the molar mass of each compound.

a. 92.45 g/mol

b. 135.04 g/mol

c. 44.01 g/mol

d. 40.06 g/mol

6. For each compound, write the condensed formula, name the compound, and give its molar mass.

a. $C_5H_{10}O_2$, Valeric Acid, 102.13 g/mol

b. H_3PO_3, Phosphorous acid, 82 g/mol

7. For each compound, write the condensed formula, name the compound, and give its molar mass.

a. $C_2H_5NH_2$, Ethylamine, 45.08 g/mol

b. HIO_3, Iodic acid, 175.91 g/mol

8. Calculate the number of moles in 5.00×10^2 g of each substance. How many molecules or formula units are present in each sample?

a. 5.37×10^{24} mol

b. 3.01×10^{24} mol

c. 8.80×10^{23} mol

d. 4.04×10^{24} mol

e. 6.84×10^{24} mol

9. Calculate the mass in grams of each sample.

a. 47.85 grams

b. 384.52 grams

c. 536.57 grams

10. Give the number of molecules or formula units in each sample.

a. 7.83×10^{21} molecules

b. 6.20×10^{23} molecules

c. 1.60×10^{23} molecules

11. Give the number of moles in each sample.

a. 1590.8 moles

b. 6011.3 moles

c. 115244.1 moles

12. Solutions of iodine are used as antiseptics and disinfectants. How many iodine atoms correspond to 11.0 g of molecular iodine (I_2)?

2.61×10^{22} molecules

13. What is the total number of atoms in each sample?

a. 2.60×10^{23} atoms

b. 1.01×10^{25} atoms

c. 1.09×10^{23} atoms

d. 2.41×10^{24} atoms

14. What is the total number of atoms in each sample?

a. 5.9×10^{23} atoms

b. 2.8×10^{24} atoms

c. 3.31×10^{24} atoms

d. 8.15×10^{24} atoms

15. What is the total number of atoms in each sample?

a. 3.69×10^{22} atoms

b. 1.13×10^{23} atoms

c. 8.54×10^{22} atoms

d. 3.50×10^{23} atoms

16.

a. False, the number of molecules in 0.5 mol Cl2 are the same amount of molecules in H2

b. False, the number of molecules in H2 is 2 x (6.022 x10^23) H atoms

c. True, 2 H (1.01 amu) + 1 O (16.01) = 18.0 amu

d. True, C6H6 -> 12(6) + 1(6) = 78 amu

17. Complete the following table

a. 0.39

b. 2.36x10^23

c. 7.08x10^23

d. 482.8

e. 1.71x10^24

f. 8.55x10^24

g. 7932.7

h. 148.3

i. 5.36x10^26

j. 46938.5

k. 425.7

l. 1276.98

m. 126.5

n. 7.77x10^23

o. 5.44x10^24

p. 0.14

q. 8.27x10^22

r. 1.65x10^24

s. 34358

t. 406.8

u. 1.23x10^2

18. Give the formula mass or the molecular mass of each substance.

a. 261.67 amu
b. 301.04 amu
c. 286.98 amu
d. 551.73 amu

19. Give the formula mass or the molecular mass of each substance.

a. 273.21 amu
b. 69.62 amu
c. 330.04 amu
d. 426.99 amu

3.6: Empirical Formulas from Analysis

3.6: Quantitative Information from Balanced Equations

Conceptual Problems

1. What information is required to determine the mass of solute in a solution if you know the molar concentration of the solution?

Numerical Problems

1. Refer to the Breathalyzer test described in Example 8. How much ethanol must be present in 89.5 mL of a person's breath to consume all the potassium dichromate in a Breathalyzer ampul containing 3.0 mL of a 0.40 mg/mL solution of potassium dichromate?
2. Phosphoric acid and magnesium hydroxide react to produce magnesium phosphate and water. If 45.00 mL of 1.50 M phosphoric acid are used in the reaction, how many grams of magnesium hydroxide are needed for the reaction to go to completion?
3. Barium chloride and sodium sulfate react to produce sodium chloride and barium sulfate. If 50.00 mL of 2.55 M barium chloride is used in the reaction, how many grams of sodium sulfate are needed for the reaction to go to completion?
4. How many grams of sodium phosphate are obtained in solution from the reaction of 75.00 mL of 2.80 M sodium carbonate with a stoichiometric amount of phosphoric acid? The second product is water; what is the third product? How many grams of the third product are obtained?
5. How many grams of ammonium bromide are produced from the reaction of 50.00 mL of 2.08 M iron(II) bromide with a stoichiometric amount of ammonium sulfide? What is the second product? How many grams of the second product are produced?

Conceptual Answers

1. The information required to determine the mass of the solution with a known molar concentration are the molar mass of the solute and the volume of the solute.

Numerical Answers

1. Refer to the Breathalyzer test described in Example 8. How much ethanol must be present in 89.5 mL of a person's breath to consume all the potassium dichromate in a Breathalyzer ampul containing 3.0 mL of a 0.40 mg/mL solution of potassium dichromate?
2. 5.905 g $Mg(OH)_2$
3. 18.105 g Na_2SO_4
4. Third Product: CO_2, Grams of Third Product: 9.24 g, Grams of Sodium Phosphate: 22.26g
5. Grams Produced: 20.37 grams NH_4Br_2, Second Product: Iron (II) Sulfide, 9.15 grams FeS

3.7: LIMITING REACTANTS

Conceptual Problems

1. Engineers use conservation of mass, called a "mass balance," to determine the amount of product that can be obtained from a chemical reaction. Mass balance assumes that the total mass of reactants is equal to the total mass of products. Is this a chemically valid practice? Explain your answer.
2. Given the equation

$$2H_{2\ (g)} + O_{2\ (g)} \rightarrow 2H + 2O_{(g)}, \tag{3.E.1}$$

   is it correct to say that 10 g of hydrogen will react with 10 g of oxygen to produce 20 g of water vapor?
3. What does it mean to say that a reaction is stoichiometric?

4. When sulfur is burned in air to produce sulfur dioxide, what is the limiting reactant? Explain your answer.
5. Is it possible for the percent yield to be greater than the theoretical yield? Justify your answer.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 2 () before proceeding to the Numerical Problems.

12. Write a balanced chemical equation for each reaction and then determine which reactant is in excess.

a. 2.46 g barium(s) plus 3.89 g bromine(l) in water to give barium bromide

b. 1.44 g bromine(l) plus 2.42 g potassium iodide(s) in water to give potassium bromide and iodine

c. 1.852 g of Zn metal plus 3.62 g of sulfuric acid in water to give zinc sulfate and hydrogen gas

d. 0.147 g of iron metal reacts with 0.924 g of silver acetate in water to give iron(II) acetate and silver metal

e. 3.142 g of ammonium phosphate reacts with 1.648 g of barium hydroxide in water to give ammonium hydroxide and barium phosphate

13. Under the proper conditions, ammonia and oxygen will react to form dinitrogen monoxide (nitrous oxide, also called laughing gas) and water. Write a balanced chemical equation for this reaction. Determine which reactant is in excess for each combination of reactants.

a. 24.6 g of ammonia and 21.4 g of oxygen

b. 3.8 mol of ammonia and 84.2 g of oxygen

c. 3.6×10^{24} molecules of ammonia and 318 g of oxygen

d. 2.1 mol of ammonia and 36.4 g of oxygen

14. When a piece of zinc metal is placed in aqueous hydrochloric acid, zinc chloride is produced, and hydrogen gas is evolved. Write a balanced chemical equation for this reaction. Determine which reactant is in excess for each combination of reactants.

a. 12.5 g of HCl and 7.3 g of Zn

b. 6.2 mol of HCl and 100 g of Zn

c. 2.1×10^{23} molecules of Zn and 26.0 g of HCl

d. 3.1 mol of Zn and 97.4 g of HCl

15. Determine the mass of each reactant needed to give the indicated amount of product. Be sure that the chemical equations are balanced.

a. $NaI(aq) + Cl_2(g) \rightarrow NaCl(aq) + I_2(s)$; 1.0 mol of NaCl

b. $NaCl(aq) + H_2SO_4(aq) \rightarrow HCl(g) + Na_2SO_4(aq)$; 0.50 mol of HCl

c. $NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$; 1.5 mol of HNO_3

16. Determine the mass of each reactant needed to give the indicated amount of product. Be sure that the chemical equations are balanced.

a. $AgNO_3(aq) + CaCl_2(s) \rightarrow AgCl(s) + Ca(NO_3)_2(aq)$; 1.25 mol of AgCl

b. $Pb(s) + PbO_2(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2O(l)$; 3.8 g of $PbSO_4$

c. $H_3PO_4(aq) + MgCO_3(s) \rightarrow Mg_3(PO_4)_2(s) + CO_2(g) + H_2O(l)$; 6.41 g of $Mg_3(PO_4)_2$

17. Determine the percent yield of each reaction. Be sure that the chemical equations are balanced. Assume that any reactants for which amounts are not given are in excess. (The symbol Δ indicates that the reactants are heated.)

a. $KClO_3(s) \xrightarrow{\Delta} KCl(s)+O_2(g)$;2.14 g of $KClO_3$ produces 0.67 g of O_2

b. $Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + SO_2(g) + H_2O(l)$; 4.00 g of copper gives 1.2 g of sulfur dioxide

c. $AgC_2H_3O_2(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + NaC_2H_3O_2(aq)$; 5.298 g of silver acetate produces 1.583 g of silver phosphate

18. Each step of a four-step reaction has a yield of 95%. What is the percent yield for the overall reaction?

19. A three-step reaction yields of 87% for the first step, 94% for the second, and 55% for the third. What is the percent yield of the overall reaction?

20. Give a general expression relating the theoretical yield (in grams) of product that can be obtained from x grams of B, assuming neither A nor B is limiting.

$A + 3B \rightarrow 2C$

21. Under certain conditions, the reaction of hydrogen with carbon monoxide can produce methanol.

a. Write a balanced chemical equation for this reaction.

b. Calculate the percent yield if exactly 200 g of methanol is produced from exactly 300 g of carbon monoxide.

22. Chlorine dioxide is a bleaching agent used in the paper industry. It can be prepared by the following reaction:

$NaClO_2(s) + Cl_2(g) \rightarrow ClO_2(aq) + NaCl(aq)$

a. What mass of chlorine is needed for the complete reaction of 30.5 g of $NaClO_2$?

b. Give a general equation for the conversion of x grams of sodium chlorite to chlorine dioxide.

23. The reaction of propane gas ($CH_3CH_2CH_3$) with chlorine gas (Cl_2) produces two monochloride products: $CH_3CH_2CH_2Cl$ and $CH_3CHClCH_3$. The first is obtained in a 43% yield and the second in a 57% yield.

a. If you use 2.78 g of propane gas, how much chlorine gas would you need for the reaction to go to completion?

b. How many grams of each product could theoretically be obtained from the reaction starting with 2.78 g of propane?

c. Use the actual percent yield to calculate how many grams of each product would actually be obtained.

24. Protactinium (Pa), a highly toxic metal, is one of the rarest and most expensive elements. The following reaction is one method for preparing protactinium metal under relatively extreme conditions:

$$2\,PaI_5\,(s) \xrightarrow{\Delta} 2\,Pa\,(s) + 5\,I_2\,(s)$$

a. Given 15.8 mg of reactant, how many milligrams of protactinium could be synthesized?

b. If 3.4 mg of Pa was obtained, what was the percent yield of this reaction?

c. If you obtained 3.4 mg of Pa and the percent yield was 78.6%, how many grams of PaI5 were used in the preparation?

25. Aniline ($C_6H_5NH_2$) can be produced from chlorobenzene (C_6H_5Cl) via the following reaction:

$C_6H_5Cl(l) + 2NH_3(g) \rightarrow C_6H_5NH_2(l) + NH_4Cl(s)$

Assume that 20.0 g of chlorobenzene at 92% purity is mixed with 8.30 g of ammonia.

a. Which is the limiting reactant?

b. Which reactant is present in excess?

c. What is the theoretical yield of ammonium chloride in grams?

d. If 4.78 g of NH_4Cl was recovered, what was the percent yield?

e. Derive a general expression for the theoretical yield of ammonium chloride in terms of grams of chlorobenzene reactant, if ammonia is present in excess.

26. A stoichiometric quantity of chlorine gas is added to an aqueous solution of NaBr to produce an aqueous solution of sodium chloride and liquid bromine. Write the chemical equation for this reaction. Then assume an 89% yield and calculate the mass of chlorine given the following:

a. 9.36×10^{24} formula units of NaCl

b. 8.5×10^{4} mol of Br_2

c. 3.7×10^{8} g of NaCl

Conceptual Answers

1. It is not a chemically valid practice because the law of conservation of mass applies to closed/isolated systems only, so in this case of an open system converting mass into energy and allowing it to escape the system wouldn't be valid.
2. No it is not correct because in order to examine the molecular weight you need to take log of both molecules to see what there true weight is. In this case, log of O2 = 10g/(32 g/mol) = 0.3125 g/mol while log of H2 = 10g/(2 g/mol) = 5 g/mol. With that when hydrogen and oxygen react against each other ((2 x (0.3125 g/L)) x (18 g/mol H2O)) = 11.25 g of water vapor
3. When a reaction is stoichiometric it means that the none of the reactants remain after being introduced leaving no excess or total leaving quantity.
4. From a reaction of S + O_2 -> SO_2 we're able to determine that the limiting reactant would be sulfur because the amount of O_2 in the air is higher than the amount of sulfur that is burned in the reaction.
5. Yes it is possible, given the equation of: percent yield = (actual yield)/(Theoretical Yield) its entirely possible to have the percent yield become greater than the theoretical yield when the product of the reaction has impurities that increase the mass compared if the product was pure.

Numerical Answers

12. Write a balanced chemical equation for each reaction and then determine which reactant is in excess.

a. $Ba(s) + Br_2(l) = BaBr_2(aq)$

Reactant in excess: Br_2

b. $Br_2(l) + 2KI(s) = 2KBr + I_2$

Reactant in Excess: Br_2

c. $Zn + H_2SO_4 = ZnSO_4 + H_2$

Reactant in excess: H_2SO_4

d. $Fe + 2\ AgC_2H_3O_2 = Fe(C_2H_3O_2)_2 + 2\ Ag$

Reactant in excess: $AgC_2H_3O_2$

e. $2\ (NH_4)_3PO_4 + 3\ Ba(OH)_2 = 6\ NH_4OH + Ba_3(PO_4)_2$

Reactant in excess: $Ba(OH)_2$

13. The balanced chemical equation for this reaction is

$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$

a. NH_3

b. NH_3

c. O_2

d. NH_3

14. a. Excess: HCl

b. Excess: HCl

c. Excess: HCl

d. Excess: Zn

15.

a. 150 g NaI and 35 g Cl_2

b. 29 g NaCl and 25 g H_2SO_4

c. 140 g NO_2 and 27 g H_2O

16.

a. $2\ AgNO_3(aq) + CaCl_2(s) = 2\ AgCl(s) + Ca(NO_3)_2(aq)$; Mass of Reactant: 212.34g AgNO3 and 69.4 g CaCl2

b. $Pb(s) + PbO_2(s) + 2\ H_2SO_4(aq) = 2\ PbSO_4(s) + 2\ H_2O(l)$; Mass of Reactant: 1.3g Pb, 1.5g PbO_2, 1.2g H_2SO_4

c. $2\ H_3PO_4(aq) + 3\ MgCO_3(s) = Mg_3(PO_4)_2(s) + 3\ CO_2(g) + 3\ H_2O(l)$; Mass of Reactant: 6.17 g of $MgCO_3$, 4.78g of H_3PO_4

17.

a. 80%

b. 30%

c. 35.7%

18. 81%

19. 45%.

20. (x/molecular mass of B) x (2/3) x (molecular mass of C)

21.

a. $CO + 2H_2 \rightarrow CH_3OH$

b. 58.28%

22. 2 $NaClO_2(s) + Cl_2(g) \rightarrow ClO_2(aq) + NaCl(aq)$

a. 11.9 g Cl_2

b. (0.7458g= Grams of ClO2 = (x/(90.44 g/mol)) x (2/2) x (67.45 g ClO2/ 1 mol ClO2

23.

a. 2.24 g Cl_2

b. 4.95 g

c. 2.13 g $CH_3CH_2CH_2Cl$ plus 2.82 g $CH_3CHClCH_3$

24. a. 4.14mg Pa

b. 82.1%

c. 0.0162 g PaI5

25.

a. chlorobenzene

b. ammonia

c. 8.74 g ammonium chloride.

d. 55%

e. $Theoretical\ yield\ (NH_4Cl) = \frac{mass\ of\ chlorobenzene\ (g) \times 0.92 \times \times 53.49\ g/mol}{112.55\ g/mol}$

26.

a. 6619.19g Cl_2

b. 6.77 x 10^6 g Cl_2

c. 2.52 x 10^8 g Cl_2

Conceptual Problems II

1. Engineers use conservation of mass, called a “mass balance,” to determine the amount of product that can be obtained from a chemical reaction. Mass balance assumes that the total mass of reactants is equal to the total mass of products. Is this a chemically valid practice? Explain your answer.
2. Given the equation

$$2H_{2\ (g)} + O_{2\ (g)} \rightarrow 2H + 2O_{(g)}, \tag{3.E.2}$$

   is it correct to say that 10 g of hydrogen will react with 10 g of oxygen to produce 20 g of water vapor?
3. What does it mean to say that a reaction is stoichiometric?
4. When sulfur is burned in air to produce sulfur dioxide, what is the limiting reactant? Explain your answer.
5. Is it possible for the percent yield to be greater than the theoretical yield? Justify your answer.

Numerical Problems II

Please be sure you are familiar with the topics discussed in Essential Skills 2 () before proceeding to the Numerical Problems.

17. Determine the percent yield of each reaction. Be sure that the chemical equations are balanced. Assume that any reactants

for which amounts are not given are in excess. (The symbol Δ indicates that the reactants are heated.)

a. $KClO_3(s) \xrightarrow{\Delta} KCl(s)+O_2(g)$;2.14 g of $KClO_3$ produces 0.67 g of O_2

b. $Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + SO_2(g) + H_2O(l)$; 4.00 g of copper gives 1.2 g of sulfur dioxide

c. $AgC_2H_3O_2(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + NaC_2H_3O_2(aq)$; 5.298 g of silver acetate produces 1.583 g of silver phosphate

18. Each step of a four-step reaction has a yield of 95%. What is the percent yield for the overall reaction?

19. A three-step reaction yields of 87% for the first step, 94% for the second, and 55% for the third. What is the percent yield of the overall reaction?

20. Give a general expression relating the theoretical yield (in grams) of product that can be obtained from x grams of B, assuming neither A nor B is limiting.

$A + 3B \rightarrow 2C$

21. Under certain conditions, the reaction of hydrogen with carbon monoxide can produce methanol.

a. Write a balanced chemical equation for this reaction.

b. Calculate the percent yield if exactly 200 g of methanol is produced from exactly 300 g of carbon monoxide.

22. Chlorine dioxide is a bleaching agent used in the paper industry. It can be prepared by the following reaction:

$NaClO_2(s) + Cl_2(g) \rightarrow ClO_2(aq) + NaCl(aq)$

a. What mass of chlorine is needed for the complete reaction of 30.5 g of $NaClO_2$?

b. Give a general equation for the conversion of x grams of sodium chlorite to chlorine dioxide.

23. The reaction of propane gas ($CH_3CH_2CH_3$) with chlorine gas (Cl_2) produces two monochloride products: $CH_3CH_2CH_2Cl$ and $CH_3CHClCH_3$. The first is obtained in a 43% yield and the second in a 57% yield.

a. If you use 2.78 g of propane gas, how much chlorine gas would you need for the reaction to go to completion?

b. How many grams of each product could theoretically be obtained from the reaction starting with 2.78 g of propane?

c. Use the actual percent yield to calculate how many grams of each product would actually be obtained.

24. Protactinium (Pa), a highly toxic metal, is one of the rarest and most expensive elements. The following reaction is one method for preparing protactinium metal under relatively extreme conditions:

$$2PaI_5(s) \xrightarrow{\Delta} 2Pa(s) + 5I_2(s) \tag{3.E.3}$$

a. Given 15.8 mg of reactant, how many milligrams of protactinium could be synthesized?

b. If 3.4 mg of Pa was obtained, what was the percent yield of this reaction?

c. If you obtained 3.4 mg of Pa and the percent yield was 78.6%, how many grams of PaI5 were used in the preparation?

25. Aniline ($C_6H_5NH_2$) can be produced from chlorobenzene (C_6H_5Cl) via the following reaction:

$C_6H_5Cl(l) + 2NH_3(g) \rightarrow C_6H_5NH_2(l) + NH_4Cl(s)$

Assume that 20.0 g of chlorobenzene at 92% purity is mixed with 8.30 g of ammonia.

a. Which is the limiting reactant?

b. Which reactant is present in excess?

c. What is the theoretical yield of ammonium chloride in grams?

d. If 4.78 g of NH_4Cl was recovered, what was the percent yield?

e. Derive a general expression for the theoretical yield of ammonium chloride in terms of grams of chlorobenzene reactant, if ammonia is present in excess.

26. A stoichiometric quantity of chlorine gas is added to an aqueous solution of NaBr to produce an aqueous solution of sodium chloride and liquid bromine. Write the chemical equation for this reaction. Then assume an 89% yield and calculate the mass of chlorine given the following:

a. 9.36×10^{24} formula units of NaCl

b. 8.5×10^{4} mol of Br_2

c. 3.7×10^{8} g of NaCl

Numerical Answers II

17.

a. 80%

b. 30%

c. 35.7%

19. 45%.

21.

a. $CO + 2H_2 \rightarrow CH_3OH$

b. 58.28%

23.

a. 2.24 g Cl_2

b. 4.95 g

c. 2.13 g $CH_3CH_2CH_2Cl$ plus 2.82 g $CH_3CHClCH_3$

25.

a. chlorobenzene

b. ammonia

c. 8.74 g ammonium chloride.

d. 55%

e. $Theoretical\ yield\ (NH_4Cl) = \frac{mass\ of\ chlorobenzene\ (g) \times 0.92 \times \times 53.49\ g/mol}{112.55\ g/mol}$

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3.S: Stoichiometry (Summary)

- atoms are neither created nor destroyed during any chemical reaction
- **stoichiometry** – quantitative nature of chemical formulas and chemical reactions

3.1: Chemical Equations

A chemical reaction is described by a chemical equation that gives the identities and quantities of the reactants and the products. In a chemical reaction, one or more substances are transformed to new substances. A chemical reaction is described by a chemical equation, an expression that gives the identities and quantities of the substances involved in a reaction. A chemical equation shows the starting compound(s)—the reactants—on the left and the final compound(s)—the products—on the right.

- chemical equations – the way chemical reactions are represented
- **reactants** – starting substances
- **products** – substances produced from a reaction
- **balanced equation** – equation with equal atoms on both sides of the equation
- subscripts should never be changed in balancing an equation
- coefficients changes only the amount and not identity of the substance

3.2: Some Simple Patterns of Chemical Reactivity

By recognizing general patterns of chemical reactivity, you will be able to successfully predict the products formed by a given combination of reactants We can often predict a reaction if we have seen a similar reaction before.

3.2.1 Using the Periodic Table

- periodic table can be used to determine reactivity of substances
- all alkali metals react with water to form their hydroxide compounds and hydrogen

3.2.2 Combustion in Air

- ◦ rapid reaction that produces a flame
  ◦ most combustion reactions in air involve oxygen
  ◦ hydrocarbons and related compounds produce CO_2 and H_2O during combustion

3.2.3 Combination and Decomposition Reactions

- ◦ combination reactions two or more substances react to form one product
  ◦ decomposition reaction one substance produces two or more substances

3.3: Formula Masses

The empirical formula of a substance can be calculated from its percent composition, and the molecular formula can be determined from the empirical formula and the compound's molar mass. The empirical formula of a substance can be calculated from the experimentally determined percent composition, the percentage of each element present in a pure substance by mass. In many cases, these percentages can be determined by combustion analysis.

3.3.1 The Atomic Mass Scale

- **atomic mass unit (amu)** – unit in measuring mass of atoms
- 1 amu = $1.66054*10^{-24}$g and 1 amu = $6.02214*10^{24}$amu

3.3.2 Average Atomic Masses

- **atomic weight –** average atomic mass

3.3.3 Formula and Molecular Weights

- **formula weight** – sum of the atomic weights of each atom in its chemical formula
- **molecular weight** – same as formula weight

3.3.4 Percentage composition from Formulas

- ◦ ((atoms of element)(AW)/(FW of compound) * 100

3.3.5 The Mole

- **avogadro's number** – $6.02*10^{23}$ atoms
- **molar mass** – numerically equal to its formula weight
- grams moles molecules

3.5: Empirical Formulas from Analysis

Molecular formulas tell you how many atoms of each element are in a compound, and empirical formulas tell you the simplest or most reduced ratio of elements in a compound. If a compound's molecular formula cannot be reduced any more, then the empirical formula is the same as the molecular formula. Combustion analysis can determine the empirical formula of a compound, but cannot determine the molecular formula (other techniques can though).

- empirical formula gives relative number of atoms in each element
- **mass % elements** >>> assume 100g sample >>> **grams of each element** >>> use atomic weights >>> **moles of each element** >>> calculate mole ratio >>> **empirical formula**
- "percent to mass, mass to mol, divide by small, multiply 'til whole/"

3.5.1 Molecular Formula from Empirical Formula

- ◦ the subscripts in the molecular formula of a substance are always a whole-number multiple of the corresponding subscripts in its empirical formula

3.5.2 Combustion Analysis

3.6: Quantitative Information from Balanced Equations

Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in the balanced chemical equation. Quantitative calculations that involve the stoichiometry of reactions in solution use volumes of solutions of known concentration instead of masses of reactants or products. The coefficients in the balanced chemical equation tell how many moles of reactants are needed and how many moles of product can be produced.

- the coefficients in a balanced chemical equation can be interpreted both as the relative numbers of molecules involved in the reaction and as the relative numbers of moles
- stoichiometrically equivalent quantities
- grams reactant >> moles reactant >> moles product >> grams product
- grams of substance A >> use molar mass of A >> moles of substance A >> use coefficients of A and B from balanced equation >> moles of substance B >> use molar mass of B >> grams of substance B

3.7: Limiting Reactants

The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained. The stoichiometry of a reaction describes the relative amounts of reactants and products in a balanced chemical equation. A stoichiometric quantity of a reactant is the amount necessary to react completely with the other reactant(s). If a reactant remains unconsumed after complete reaction has occurred, it is in excess. The reactant that is consumed first is the limiting reagent.

- **limiting reactant** – limits the amount of product formed

3.7.1 Theoretical Yields

- theoretical yield – the amount of product that is calculated to form
- actual yield – the amount of product actually formed

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

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4: REACTIONS IN AQUEOUS SOLUTION

A solution is a homogeneous mixture in which substances present in lesser amounts, called solutes, are dispersed uniformly throughout the substance in the greater amount, the solvent. An aqueous solution is a solution in which the solvent is water, whereas in a nonaqueous solution, the solvent is a substance other than water. Familiar examples of nonaqueous solvents are ethyl acetate, used in nail polish removers, and turpentine, used to clean paint brushes. In this chapter, we focus on reactions that occur in aqueous solution.

There are many reasons for carrying out reactions in solution. For a chemical reaction to occur, individual atoms, molecules, or ions must collide, and collisions between two solids, which are not dispersed at the atomic, molecular, or ionic level, do not occur at a significant rate. In addition, when the amount of a substance required for a reaction is so small that it cannot be weighed accurately, using a solution of that substance, in which the solute is dispersed in a much larger mass of solvent, enables chemists to measure its quantity with great precision. Chemists can also more effectively control the amount of heat consumed or produced in a reaction when the reaction occurs in solution, and sometimes the nature of the reaction itself can be controlled by the choice of solvent.

This chapter introduces techniques for preparing and analyzing aqueous solutions, for balancing equations that describe reactions in solution, and for solving problems using solution stoichiometry. By the time you complete this chapter, you will know enough about aqueous solutions to explain what causes acid rain, why acid rain is harmful, and how a Breathalyzer measures alcohol levels. You will also understand the chemistry of photographic development, be able to explain why rhubarb leaves are toxic, and learn about a possible chemical reason for the decline and fall of the Roman Empire.

4.1: General Properties of Aqueous Solutions

4.2: Precipitation Reactions

4.3: Acid-Base Reactions

4.4: Oxidation-Reduction Reactions

4.5: Concentration of Solutions

4.6: Solution Stoichiometry and Chemical Analysis

4.E: Reactions in Aqueous Solution (Exercises)

4.S: Reactions in Aqueous Solution (Summary)

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4.1: General Properties of Aqueous Solutions

Learning Objectives

- To understand how and why solutions form

The solvent in aqueous solutions is water, which makes up about 70% of the mass of the human body and is essential for life. Many of the chemical reactions that keep us alive depend on the interaction of water molecules with dissolved compounds. Moreover, the presence of large amounts of water on Earth's surface helps maintain its surface temperature in a range suitable for life. In this section, we describe some of the interactions of water with various substances and introduce you to the characteristics of aqueous solutions.

Polar Substances

As shown in Figure 4.1.1, the individual water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. As is typical of group 16 elements, the oxygen atom in each O–H covalent bond attracts electrons more strongly than the hydrogen atom does. Consequently, the oxygen and hydrogen nuclei do not equally share electrons. Instead, hydrogen atoms are electron poor compared with a neutral hydrogen atom and have a partial positive charge, which is indicated by δ^+. The oxygen atom, in contrast, is more electron rich than a neutral oxygen atom, so it has a partial negative charge. This charge must be twice as large as the partial positive charge on each hydrogen for the molecule to have a net charge of zero. Thus its charge is indicated by $2\delta^-$. This unequal distribution of charge creates a polar bond in which one portion of the molecule carries a partial negative charge, while the other portion carries a partial positive charge (Figure 4.1.1). Because of the arrangement of polar bonds in a water molecule, water is described as a polar substance.

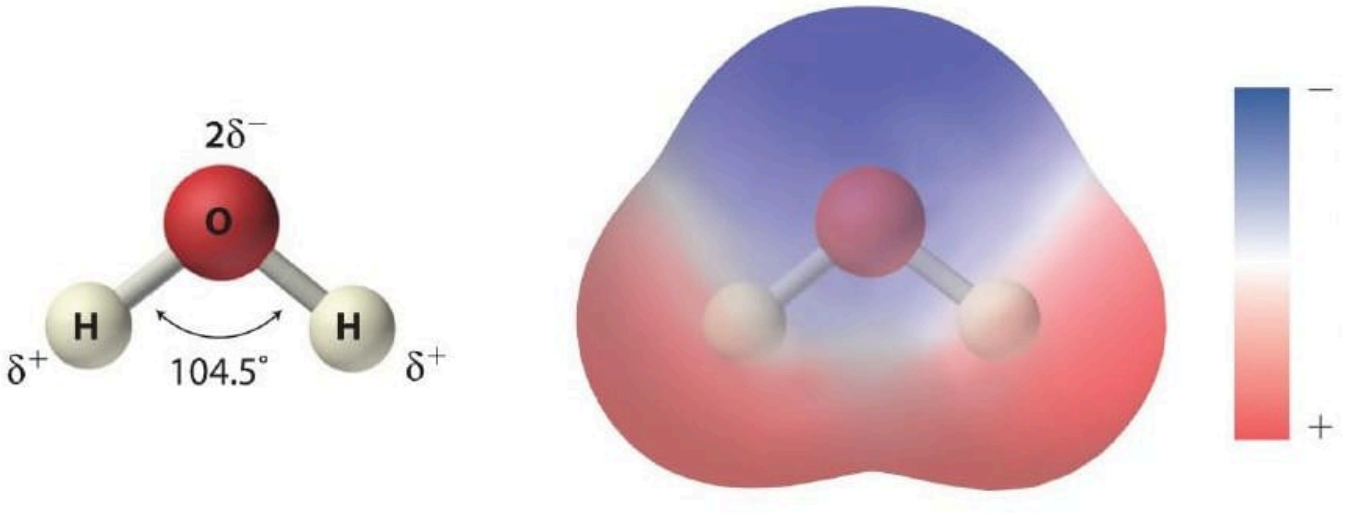


Figure 4.1.1: The Polar Nature of Water. Each water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. Because the oxygen atom attracts electrons more strongly than the hydrogen atoms do, the oxygen atom is partially negatively charged ($2\delta^-$; blue) and the hydrogen atoms are partially positively charged (δ^+; red). For the molecule to have a net charge of zero, the partial negative charge on oxygen must be twice as large as the partial positive charge on each hydrogen. (CC BY-NC-SA 3.0; Anonymous via LibreTexts)

Because of the asymmetric charge distribution in the water molecule, adjacent water molecules are held together by attractive electrostatic ($\delta^+ \ldots \delta^-$) interactions between the partially negatively charged oxygen atom of one molecule and the partially positively charged hydrogen atoms of adjacent molecules (Figure 4.1.2). Energy is needed to overcome these electrostatic attractions. In fact, without them, water would evaporate at a much lower temperature, and neither Earth's oceans nor we would exist!

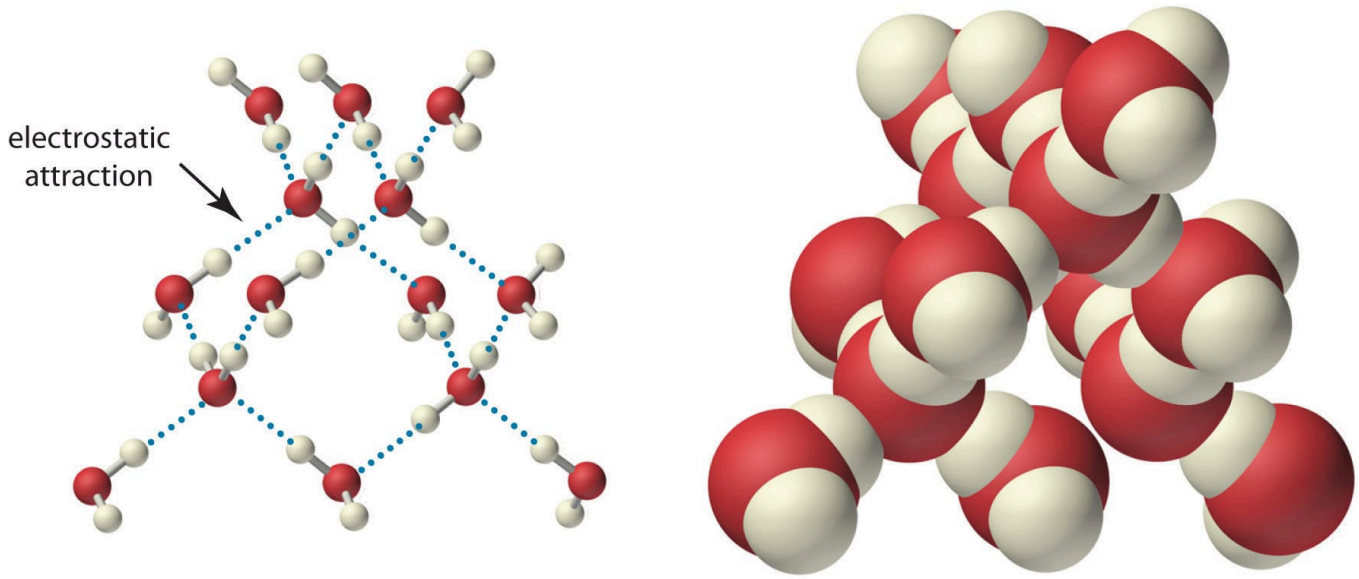


Figure 4.1.2: The Structure of Liquid Water. Two views of a water molecule are shown: (a) a ball-and-stick structure and (b) a space-filling model. Water molecules are held together by electrostatic attractions (dotted lines) between the partially negatively charged oxygen atom of one molecule and the partially positively charged hydrogen atoms on adjacent molecules. As a result, the water molecules in liquid water form transient networks with structures similar to that shown. Because the interactions between water molecules are continually breaking and reforming, liquid water does not have a single fixed structure. (CC BY-NC-SA 3.0; Anonymous via LibreTexts)

As you learned previously,, ionic compounds such as sodium chloride (NaCl) are also held together by electrostatic interactions—in this case, between oppositely charged ions in the highly ordered solid, where each ion is surrounded by ions of the opposite charge in a fixed arrangement. In contrast to an ionic solid, the structure of liquid water is not completely ordered because the interactions between molecules in a liquid are constantly breaking and reforming.

The unequal charge distribution in polar liquids such as water makes them good solvents for ionic compounds. When an ionic solid dissolves in water, the ions *dissociate*. That is, the partially negatively charged oxygen atoms of the H_2O molecules surround the cations (Na^+ in the case of NaCl), and the partially positively charged hydrogen atoms in H_2O surround the anions (Cl^-; Figure 4.1.3). Individual cations and anions that are each surrounded by their own shell of water molecules are called hydrated ions. We can describe the dissolution of NaCl in water as

$$\mathrm{NaCl\,(s)} \xrightarrow{\mathrm{H_2O\,(l)}} \mathrm{Na^+\,(aq) + Cl^-\,(aq)} \tag{4.1.1}$$

where (aq) indicates that Na^+ and Cl^- are hydrated ions.

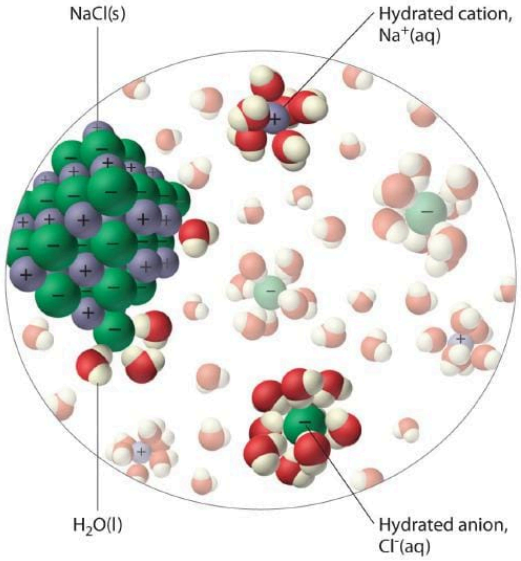


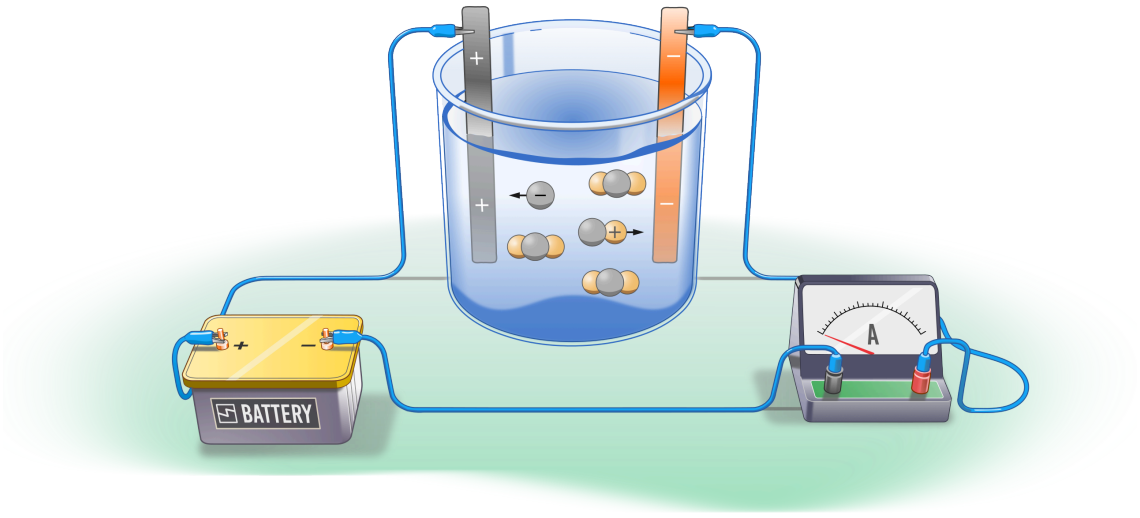
Figure 4.1.3: The Dissolution of Sodium Chloride in Water. An ionic solid such as sodium chloride dissolves in water because of the electrostatic attraction between the cations (Na^+) and the partially negatively charged oxygen atoms of water molecules, and between the anions (Cl^-) and the partially positively charged hydrogen atoms of water.(CC BY-NC-SA 3.0; Anonymous via LibreTexts)

Rule of Thumb

Polar liquids are good solvents for ionic compounds.

Electrolytes

When electricity, in the form of an *electrical potential*, is applied to a solution, ions in solution migrate toward the oppositely charged rod or plate to complete an electrical circuit, whereas neutral molecules in solution do not (Figure 4.1.4). Thus solutions that contain ions conduct electricity, while solutions that contain only neutral molecules do not. Electrical current will flow through the circuit shown in Figure 4.1.4 and the bulb will glow *only* if ions are present. The lower the concentration of ions in solution, the weaker the current and the dimmer the glow. Pure water, for example, contains only very low concentrations of ions, so it is a poor electrical conductor.



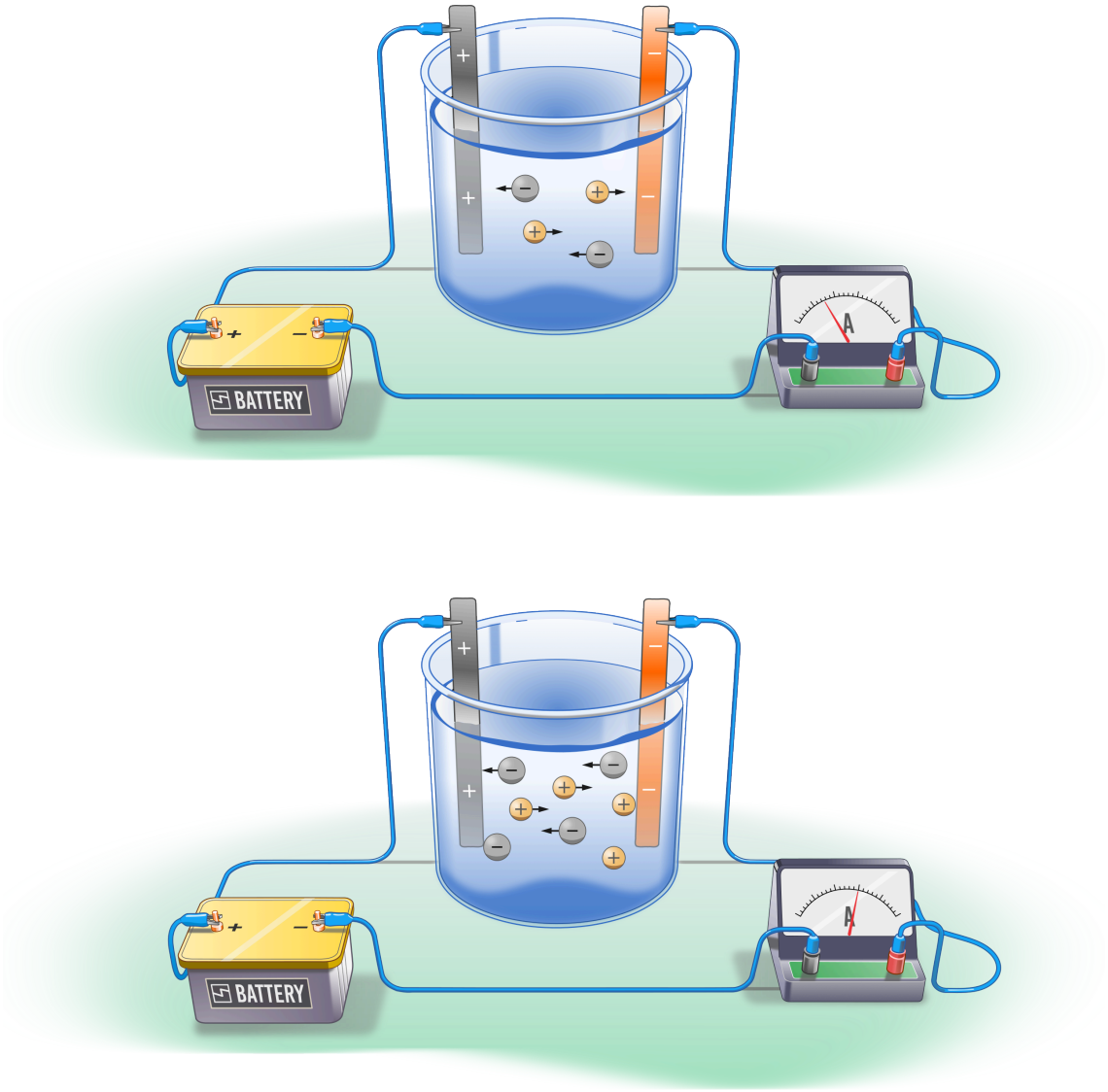


Figure 4.1.4: Comparison of three different solutions with varying amounts of ion with rods connected to a battery and current measuring device. The solution with the most ion shows greatest current measurement. Moderate ion solution shows lower reading. Very minimal ion shows no current being conducted. (CC BY 4.0; Ümit Kaya via LibreTexts)

Rule of Thumb

Solutions that contain ions conduct electricity.

An electrolyte is any compound that can form ions when dissolved in water. Electrolytes may be strong or weak. When strong electrolytes dissolve, the constituent ions dissociate completely due to strong electrostatic interactions with the solvent, producing aqueous solutions that conduct electricity very well (Figure 4.1.4). Examples include ionic compounds such as barium chloride ($\mathrm{BaCl_2}$) and sodium hydroxide (NaOH), which are both strong electrolytes and dissociate as follows:

$$\mathrm{BaCl_2\,(s)} \xrightarrow{\mathrm{H_2O\,(l)}} \mathrm{Ba^{2+}\,(aq)} + 2\,\mathrm{Cl^-\,(aq)} \tag{4.1.2}$$

$$\mathrm{NaOH\,(s)} \xrightarrow{\mathrm{H_2O\,(l)}} \mathrm{Na^+\,(aq)} + \mathrm{OH^-\,(aq)} \tag{4.1.3}$$

The single arrows from reactant to products in Equations 4.1.2 and 4.1.3 indicate that dissociation is **complete**.

When weak electrolytes dissolve, they produce relatively few ions in solution. This does *not* necessarily mean that the compounds do not dissolve readily in water; many weak electrolytes contain polar bonds and are therefore very soluble in a polar solvent such as water. They do not completely dissociate to form ions, however, because of their weaker electrostatic interactions with the solvent. Because very few of the dissolved particles are ions, aqueous solutions of weak electrolytes do not conduct electricity as well as solutions of strong electrolytes. One such compound is acetic acid (CH_3CO_2H), which contains the $-CO_2H$ unit. Although it is soluble in water, it is a weak acid and therefore also a weak electrolyte. Similarly, ammonia (NH_3) is a weak base and therefore a weak electrolyte. The behavior of weak acids and weak bases will be described in more detail later.

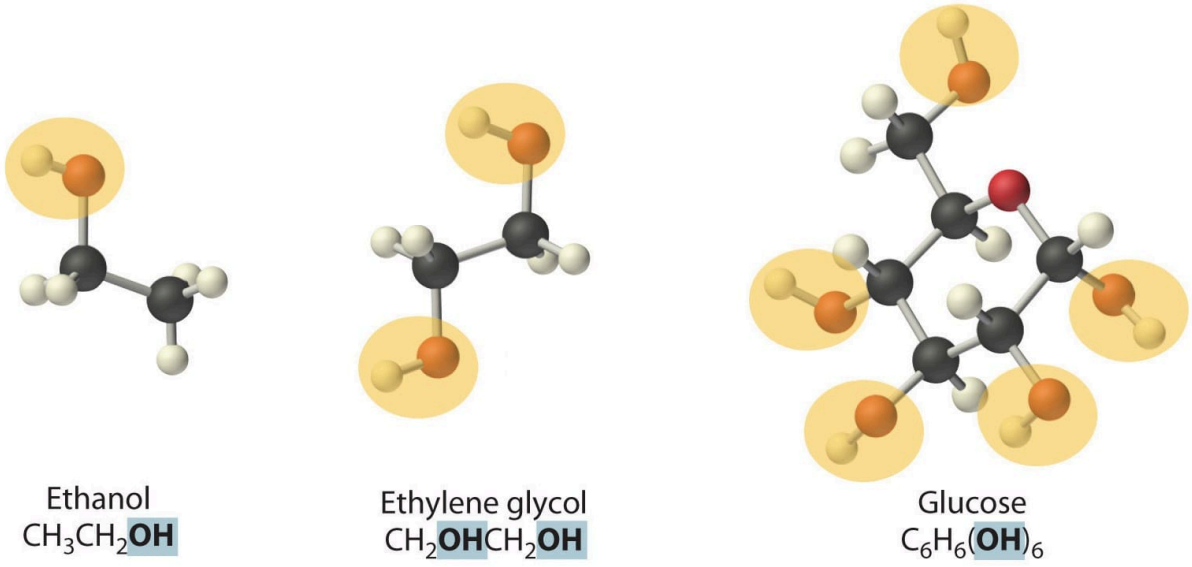
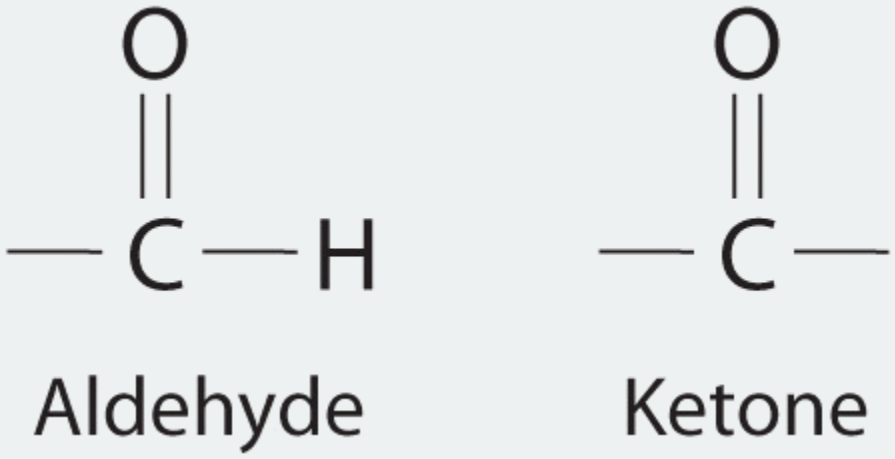


Figure 4.1.5: Ball and stick diagram of ethanol, ethylene glycol, and glucose with the oxygen hydrogen bonds highlighted in red. (CC BY-NC-SA 3.0; Anonymous via LibreTexts)

General structure of an aldehyde and a ketone

Notice that both contain the C=O group.



Nonelectrolytes (a substance that dissolves in water to form neutral molecules and has essentially no effect on electrical conductivity) that dissolve in water do so as neutral molecules and thus have essentially no effect on conductivity. Examples of nonelectrolytes that are very soluble in water but that are essentially nonconductive are ethanol, ethylene glycol, glucose, and sucrose, all of which contain the –OH group that is characteristic of alcohols (Figure 4.1.5). The topic of why alcohols and

carboxylic acids behave differently in aqueous solution is for a different Module; for now, however, you can simply look for the presence of the –OH and $-CO_2H$ groups when trying to predict whether a substance is a strong electrolyte, a weak electrolyte, or a nonelectrolyte. The distinctions between soluble and insoluble substances and between strong, weak, and nonelectrolytes are illustrated in Figure 4.1.6.

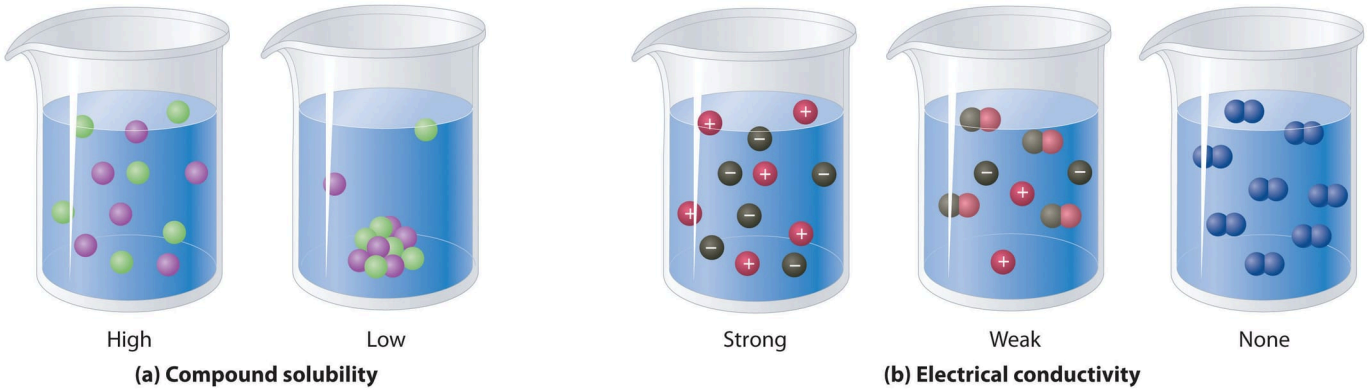


Figure 4.1.6: The Difference between Soluble and Insoluble Compounds (a) and Strong, Weak, and Nonelectrolytes (b). When a soluble compound dissolves, its constituent atoms, molecules, or ions disperse throughout the solvent. In contrast, the constituents of an insoluble compound remain associated with one another in the solid. A soluble compound is a strong electrolyte if it dissociates completely into ions, a weak electrolyte if it dissociates only slightly into ions, and a nonelectrolyte if it dissolves to produce only neutral molecules. (CC BY-NC-SA 3.0; Anonymous via LibreTexts)

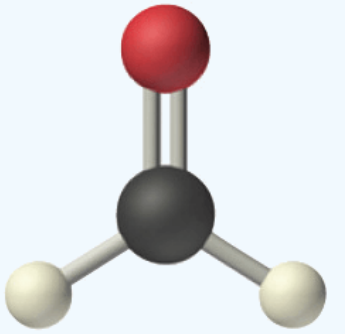
Rule of Thumb

Ionic substances and carboxylic acids are **electrolytes**; alcohols, aldehydes, and ketones are **nonelectrolytes**.

Example 4.1.1

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

a. formaldehyde



Formaldehyde, CH_2O

b. cesium chloride

Given: compound

Asked for: relative ability to form ions in water

Strategy:

A Classify the compound as ionic or covalent.

B If the compound is ionic and dissolves, it is a strong electrolyte that will dissociate in water completely to produce a solution that conducts electricity well. If the compound is covalent and organic, determine whether it contains the carboxylic acid group. If the compound contains this group, it is a weak electrolyte. If not, it is a nonelectrolyte.

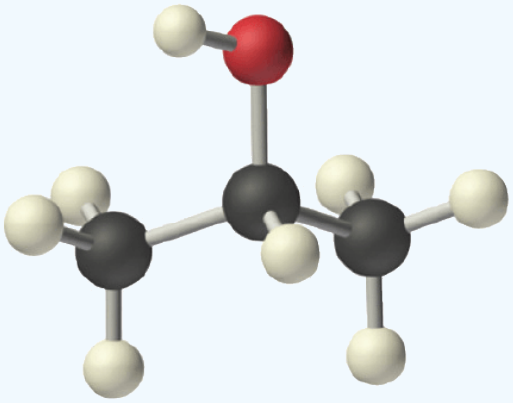
Solution:

1. **A** Formaldehyde is an organic compound, so it is covalent. **B** It contains an aldehyde group, not a carboxylic acid group, so it should be a nonelectrolyte.
2. **A** Cesium chloride (CsCl) is an ionic compound that consists of Cs^+ and Cl^- ions. **B** Like virtually all other ionic compounds that are soluble in water, cesium chloride will dissociate completely into $Cs^+(aq)$ and $Cl^-(aq)$ ions. Hence it should be a strong electrolyte.

Exercise 4.1.1

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

a. $(CH_3)_2CHOH$ (2-propanol)



2-Propanol (isopropyl alcohol), $(CH_3)_2CHOH$

b. ammonium sulfate

Answer

a. nonelectrolyte
b. strong electrolyte

Summary

Aqueous solutions can be classified as polar or nonpolar depending on how well they conduct electricity. Most chemical reactions

are carried out in *solutions*, which are homogeneous mixtures of two or more substances. In a solution, a *solute* (the substance present in the lesser amount) is dispersed in a *solvent* (the substance present in the greater amount). *Aqueous solutions* contain water as the solvent, whereas *nonaqueous solutions* have solvents other than water. Polar substances, such as water, contain asymmetric arrangements of **polar bonds**, in which electrons are shared unequally between bonded atoms. Polar substances and ionic compounds tend to be most soluble in water because they interact favorably with its structure. In aqueous solution, dissolved ions become **hydrated**; that is, a shell of water molecules surrounds them. Substances that dissolve in water can be categorized according to whether the resulting aqueous solutions conduct electricity. **Strong electrolytes** dissociate completely into ions to produce solutions that conduct electricity well. **Weak electrolytes** produce a relatively small number of ions, resulting in solutions that conduct electricity poorly. **Nonelectrolytes** dissolve as uncharged molecules and have no effect on the electrical conductivity of water.

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4.2: Precipitation Reactions

Learning Objectives

- To identify a precipitation reaction and predict solubilities.

Exchange (Double-Displacement) Reactions

A precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. We described a precipitation reaction in which a colorless solution of silver nitrate was mixed with a yellow-orange solution of potassium dichromate to give a reddish precipitate of silver dichromate:

$$\mathrm{AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \;\rightarrow Ag_2Cr_2O_7\,(s) + KNO_3\,(aq)} \tag{4.2.1}$$

This unbalanced equation has the general form of an exchange reaction:

$$\overbrace{\mathrm{AC}}^{\text{soluble}} + \overbrace{\mathrm{BD}}^{\text{soluble}} \rightarrow \underbrace{\mathrm{AD}}_{\text{insoluble}} + \overbrace{\mathrm{BC}}^{\text{soluble}} \tag{4.2.2}$$

The solubility and insoluble annotations are specific to the reaction in Equation 4.2.1 and not characteristic of all exchange reactions (e.g., both products can be soluble or insoluble). *Precipitation reactions* are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. Because both components of each compound change partners, such reactions are sometimes called *double-displacement reactions*. Two important uses of precipitation reactions are to isolate metals that have been extracted from their ores and to recover precious metals for recycling.

YouTube Video

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Video 4.2.1***:*** *Mixing Potassium Chromate and Silver Nitrate together to initiate a precipitation reaction (Equation* 4.2.1*).*

While full chemical equations show the identities of the reactants and the products and give the stoichiometries of the reactions, they are less effective at describing what is actually occurring in solution. In contrast, equations that show only the hydrated species focus our attention on the chemistry that is taking place and allow us to see similarities between reactions that might not otherwise be apparent.

Let's consider the reaction of silver nitrate with potassium dichromate above. When aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall balanced chemical equation for the reaction shows each reactant and product as undissociated, electrically neutral compounds:

$$\mathrm{2\,AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \rightarrow Ag_2Cr_2O_7\,(s) + 2\,KNO_3\,(aq)} \tag{4.2.3}$$

Although Equation 4.2.3 gives the identity of the reactants and the products, it does not show the identities of the actual species in solution. Because ionic substances such as $\mathrm{AgNO_3}$ and $\mathrm{K_2Cr_2O_7}$ are *strong electrolytes (*i.e., they dissociate completely in aqueous solution to form ions). In contrast, because $\mathrm{Ag_2Cr_2O_7}$ is not very soluble, it separates from the solution as a solid. To find out what is actually occurring in solution, it is more informative to write the reaction as a complete ionic equation showing which ions and molecules are hydrated and which are present in other forms and phases:

$$2\,\mathrm{Ag^+(aq)} + 2\,\mathrm{NO_3^-(aq)} + 2\,\mathrm{K^+(aq)} + \mathrm{Cr_2O_7^{2-}(aq)} \rightarrow \mathrm{Ag_2Cr_2O_7(s)} + 2\,\mathrm{K^+(aq)} + 2\,\mathrm{NO_3^-(aq)} \quad (4.2.4)$$

Note that $\mathrm{K^+(aq)}$ and $\mathrm{NO_3^-(aq)}$ ions are present on both sides of Equation 4.2.4 and their coefficients are the same on both sides. These ions are called *spectator ions* because they do not participate in the actual reaction. Canceling the spectator ions gives the net ionic equation, which shows only those species that participate in the chemical reaction:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \quad (4.2.5)$$

Both mass and charge must be conserved in chemical reactions because the numbers of electrons and protons do not change. For charge to be conserved, the sum of the charges of the ions multiplied by their coefficients must be the same on both sides of the equation. In Equation 4.2.5, the charge on the left side is 2(+1) + 1(−2) = 0, which is the same as the charge of a neutral $\mathrm{Ag_2Cr_2O_7}$ formula unit on the right side.

By eliminating the spectator ions, we can focus on the chemistry that takes place in a solution. For example, the overall chemical equation for the reaction between silver fluoride and ammonium dichromate is as follows:

$$2AgF(aq) + (NH_4)_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4F(aq) \quad (4.2.6)$$

The complete ionic equation for this reaction is as follows:

$$2\,\mathrm{Ag^+(aq)} + \cancel{2\,\mathrm{F^-(aq)}} + \cancel{2\,\mathrm{NH_4^+(aq)}} + \mathrm{Cr_2O_7^{2-}(aq)} \rightarrow \mathrm{Ag_2Cr_2O_7(s)} + \cancel{2\,\mathrm{NH_4^+(aq)}} + \cancel{2\,\mathrm{F^-(aq)}} \quad (4.2.7)$$

Because two $\mathrm{NH_4^+(aq)}$ and two $\mathrm{F^-(aq)}$ ions appear on both sides of Equation 4.2.7, they are spectator ions. They can therefore be canceled to give the **net ionic equation** (Equation 4.2.8), which is identical to Equation 4.2.5:

$$2\,\mathrm{Ag^+(aq)} + \mathrm{Cr_2O_7^{2-}(aq)} \rightarrow \mathrm{Ag_2Cr_2O_7(s)} \quad (4.2.8)$$

If we look at net ionic equations, it becomes apparent that many different combinations of reactants can result in the same net chemical reaction. For example, we can predict that silver fluoride could be replaced by silver nitrate in the preceding reaction without affecting the outcome of the reaction.

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Determining the Products for Precipitation Reactions: Determining the Products for Precipitation Reactions, YouTube(opens in new window) [youtu.be]

Example 4.2.1: Balancing Precipitation Equations

Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous barium nitrate with aqueous sodium phosphate to give solid barium phosphate and a solution of sodium nitrate.

Given: reactants and products

Asked for: overall, complete ionic, and net ionic equations

Strategy:

Write and balance the overall chemical equation. Write all the soluble reactants and products in their dissociated form to give the complete ionic equation; then cancel species that appear on both sides of the complete ionic equation to give the net ionic equation.

Solution:

From the information given, we can write the unbalanced chemical equation for the reaction:

$$\mathrm{Ba(NO_3)_2\,(aq) + Na_3PO_4\,(aq) \rightarrow Ba_3(PO_4)_2\,(s) + NaNO_3\,(aq)}$$

Because the product is $Ba_3(PO_4)_2$, which contains three Ba^{2+} ions and two PO_4^{3-} ions per formula unit, we can balance the equation by inspection:

$$\mathrm{3\,Ba(NO_3)_2\,(aq) + 2\,Na_3PO_4\,(aq) \rightarrow Ba_3(PO_4)_2\,(s) + 6\,NaNO_3\,(aq)}$$

This is the overall balanced chemical equation for the reaction, showing the reactants and products in their undissociated form. To obtain the complete ionic equation, we write each soluble reactant and product in dissociated form:

$$\mathrm{3\,Ba^{2+}\,(aq) + \cancel{6\,NO_3^-\,(aq)} + \cancel{6\,Na^+\,(aq)} + 2\,PO_4^{3-}\,(aq) \rightarrow Ba_3(PO_4)_2\,(s) + \cancel{6\,Na^+\,(aq)} + \cancel{6\,NO_3^-\,(aq)}}$$

The six NO_3^-(aq) ions and the six Na^+(aq) ions that appear on both sides of the equation are spectator ions that can be canceled to give the net ionic equation:

$$\mathrm{3\,Ba^{2+}\,(aq) + 2\,PO_4^{3-}\,(aq) \rightarrow Ba_3(PO_4)_2\,(s)}$$

Exercise 4.2.1: Mixing Silver Fluoride with Sodium Phosphate

Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous silver fluoride with aqueous sodium phosphate to give solid silver phosphate and a solution of sodium fluoride.

Answer available at the end of this section.

So far, we have always indicated whether a reaction will occur when solutions are mixed and, if so, what products will form. As you advance in chemistry, however, you will need to predict the results of mixing solutions of compounds, anticipate what kind of reaction (if any) will occur, and predict the identities of the products. Students tend to think that this means they are supposed to "just know" what will happen when two substances are mixed. Nothing could be further from the truth: an infinite number of chemical reactions is possible, and neither you nor anyone else could possibly memorize them all. Instead, you must begin by identifying the various reactions that *could* occur and then assessing which is the most probable (or least improbable) outcome.

The most important step in analyzing an unknown reaction is to *write down all the species—whether molecules or dissociated ions—that are actually present in the solution* (not forgetting the solvent itself) so that you can assess which species are most likely to react with one another. The easiest way to make that kind of prediction is to attempt to place the reaction into one of several familiar classifications, refinements of the five general kinds of reactions (acid–base, exchange, condensation, cleavage, and oxidation–reduction reactions). In the sections that follow, we discuss three of the most important kinds of reactions that occur in aqueous solutions: precipitation reactions (also known as exchange reactions), acid–base reactions, and oxidation–reduction reactions.

Predicting Solubilities

Table 4.2.1 gives guidelines for predicting the solubility of a wide variety of ionic compounds. To determine whether a precipitation reaction will occur, we identify each species in the solution and then refer to Table 4.2.1 to see which, if any, combination(s) of cation and anion are likely to produce an insoluble salt. In doing so, it is important to recognize that *soluble* and *insoluble* are relative terms that span a wide range of actual solubilities. We will discuss solubilities in more detail later, where you will learn that very small amounts of the constituent ions remain in solution even after precipitation of an "insoluble" salt. For our purposes, however, we will assume that precipitation of an insoluble salt is complete.

Table 4.2.1: Guidelines for Predicting the Solubility of Ionic Compounds in Water

Soluble			Exceptions
Rule 1	most salts that contain an alkali metal (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium (NH_4^+)		
Rule 2	most salts that contain the nitrate (NO_3^-) anion		
Rule 3	most salts of anions derived from monocarboxylic acids (e.g., $CH_3CO_2^-$)	but not	silver acetate and salts of long-chain carboxylates
Rule 4	most chloride, bromide, and iodide salts	but not	salts of metal ions located on the lower right side of the periodic table (e.g., Cu^+, Ag^+, Pb^{2+}, and Hg_2^{2+}).
	Insoluble		**Exceptions**
Rule 5	most salts that contain the hydroxide (OH^-) and sulfide (S^{2-}) anions	but not	salts of the alkali metals (group 1), the heavier alkaline earths (Ca^{2+}, Sr^{2+}, and Ba^{2+} in group 2), and the NH_4^+ ion.
Rule 6	most carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) salts	but not	salts of the alkali metals or the NH_4^+ ion.
Rule 7	most sulfate (SO_4^{2-}) salts that contain main group cations with a charge ≥ +2	but not	salts of +1 cations, Mg^{2+}, and dipositive transition metal cations (e.g., Ni^{2+})

Just as important as predicting the product of a reaction is knowing when a chemical reaction will *not* occur. Simply mixing solutions of two different chemical substances does *not* guarantee that a reaction will take place. For example, if 500 mL of a 1.0 M aqueous NaCl solution is mixed with 500 mL of a 1.0 M aqueous KBr solution, the final solution has a volume of 1.00 L and contains 0.50 M $Na^+(aq)$, 0.50 M $Cl^-(aq)$, 0.50 M $K^+(aq)$, and 0.50 M $Br^-(aq)$. As you will see in the following sections, none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other (Figure 4.2.1).

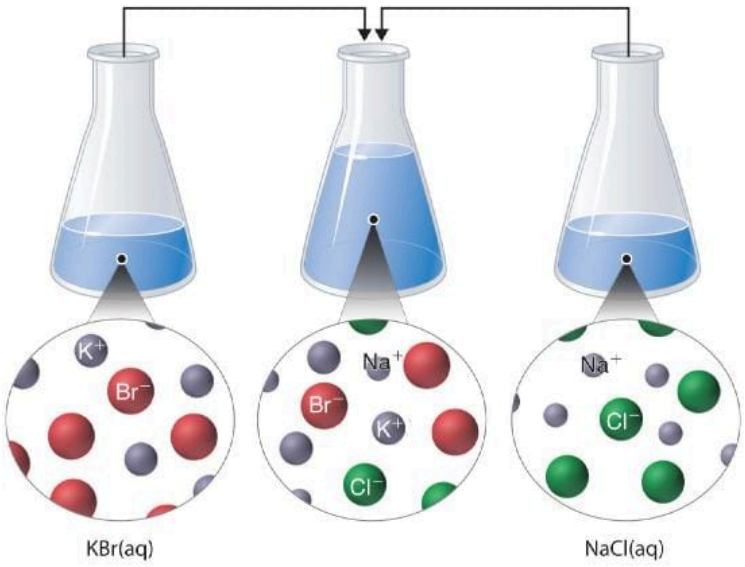


Figure 4.2.1: The Effect of Mixing Aqueous KBr and NaCl Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

Example 4.2.2

Using the information in Table 4.2.1, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

a. Aqueous solutions of barium chloride and lithium sulfate are mixed.
b. Aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.
c. Aqueous solutions of strontium bromide and aluminum nitrate are mixed.
d. Solid lead(II) acetate is added to an aqueous solution of ammonium iodide.

Given: reactants

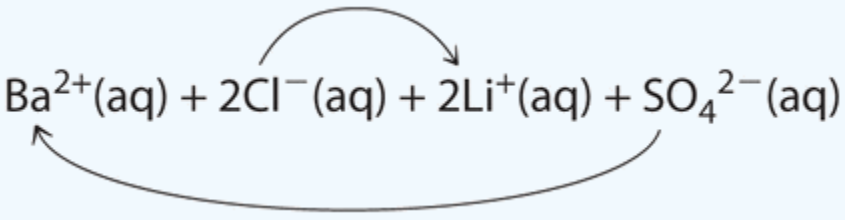
Asked for: reaction and net ionic equation

Strategy:

A. Identify the ions present in solution and write the products of each possible exchange reaction.
B. Refer to Table 4.2.1 to determine which, if any, of the products is insoluble and will therefore form a precipitate. If a precipitate forms, write the net ionic equation for the reaction.

Solution:

A Because barium chloride and lithium sulfate are strong electrolytes, each dissociates completely in water to give a solution that contains the constituent anions and cations. Mixing the two solutions *initially* gives an aqueous solution that contains Ba^{2+}, Cl^-, Li^+, and SO_4^{2-} ions. The only possible exchange reaction is to form LiCl and $BaSO_4$:



B We now need to decide whether either of these products is insoluble. Table $4.2.1$ shows that LiCl is soluble in water (rules 1 and 4), but $BaSO_4$ is not soluble in water (rule 5). Thus $BaSO_4$ will precipitate according to the net ionic equation

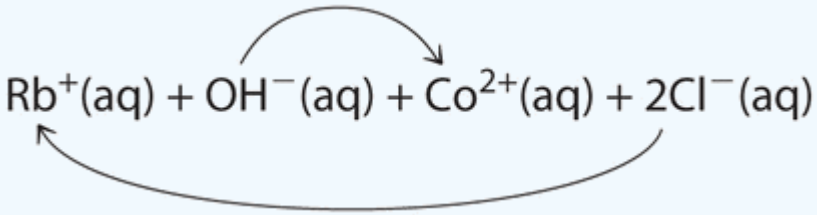
$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Although soluble barium salts are toxic, $BaSO_4$ is so insoluble that it can be used to diagnose stomach and intestinal problems without being absorbed into tissues. An outline of the digestive organs appears on x-rays of patients who have been given a "barium milkshake" or a "barium enema"—a suspension of very fine $BaSO_4$ particles in water.



An x-ray of the digestive organs of a patient who has swallowed a "barium milkshake." A barium milkshake is a suspension of very fine $BaSO_4$ particles in water; the high atomic mass of barium makes it opaque to x-rays. from Wikipedia.

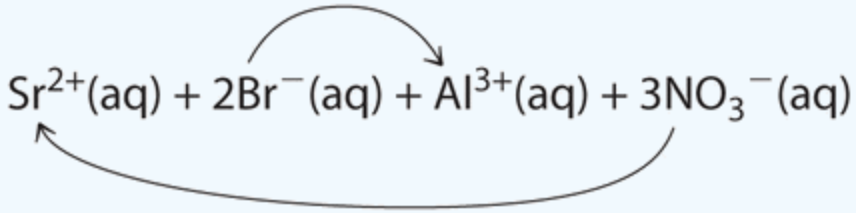
1. **A** Rubidium hydroxide and cobalt(II) chloride are strong electrolytes, so when aqueous solutions of these compounds are mixed, the resulting solution initially contains Rb^+, OH^-, Co^{2+}, and Cl^- ions. The possible products of an exchange reaction are rubidium chloride and cobalt(II) hydroxide):



   B According to Table $4.2.1$, RbCl is soluble (rules 1 and 4), but $Co(OH)_2$ is not soluble (rule 5). Hence $Co(OH)_2$ will precipitate according to the following net ionic equation:

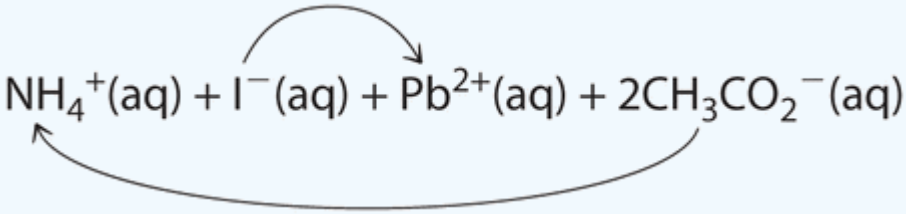
$$Co^{2+}(aq) + 2OH^-(aq) \rightarrow Co(OH)_2(s)$$

2. **A** When aqueous solutions of strontium bromide and aluminum nitrate are mixed, we initially obtain a solution that contains Sr^{2+}, Br^-, Al^{3+}, and NO_3^- ions. The two possible products from an exchange reaction are aluminum bromide and strontium nitrate:



B According to Table 4.2.1, both $AlBr_3$ (rule 4) and $Sr(NO_3)_2$ (rule 2) are soluble. Thus no net reaction will occur.

1. **A** According to Table 4.2.1, lead acetate is soluble (rule 3). Thus solid lead acetate dissolves in water to give Pb^{2+} and $CH_3CO_2^-$ ions. Because the solution also contains NH_4^+ and I^- ions, the possible products of an exchange reaction are ammonium acetate and lead(II) iodide:



B According to Table 4.2.1, ammonium acetate is soluble (rules 1 and 3), but PbI_2 is insoluble (rule 4). Thus $Pb(C_2H_3O_2)_2$ will dissolve, and PbI_2 will precipitate. The net ionic equation is as follows:

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

Exercise 4.2.2

Using the information in Table 4.2.1, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

a. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
b. Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
c. Solid sodium fluoride is added to an aqueous solution of ammonium formate.
d. Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Answer a available at the end of this section.

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Predicting the Solubility of Ionic Compounds: Predicting the Solubility of Ionic Compounds, YouTube(opens in new window) [youtu.be] (opens in new window)

Answers

Exercise 4.2.1: Mixing Silver Fluoride with Sodium Phosphate

overall chemical equation:

$$3\,\mathrm{AgF\,(aq)} + \mathrm{Na_3PO_4\,(aq)} \rightarrow \mathrm{Ag_3PO_4\,(s)} + 3\,\mathrm{NaF\,(aq)}$$

complete ionic equation:

$$3\,\mathrm{Ag^+\,(aq)} + 3\,\mathrm{F^-\,(aq)} + 3\,\mathrm{Na^+\,(aq)} + \mathrm{PO_4{}^{3-}\,(aq)} \rightarrow \mathrm{Ag_3PO_4\,(s)} + 3\,\mathrm{Na^+\,(aq)} + 3\,\mathrm{F^-\,(aq)}$$

net ionic equation:

$$3\,\mathrm{Ag^+\,(aq)} + \mathrm{PO_4{}^{3-}\,(aq)} \rightarrow \mathrm{Ag_3PO_4\,(s)}$$

Exercise 4.2.2

$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$
$2PO_4^{3-}(aq) + 3Hg^{2+}(aq) \rightarrow Hg_3(PO_4)_2(s)$
$NaF(s)$ dissolves; no net reaction
$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

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4.3: Acid-Base Reactions

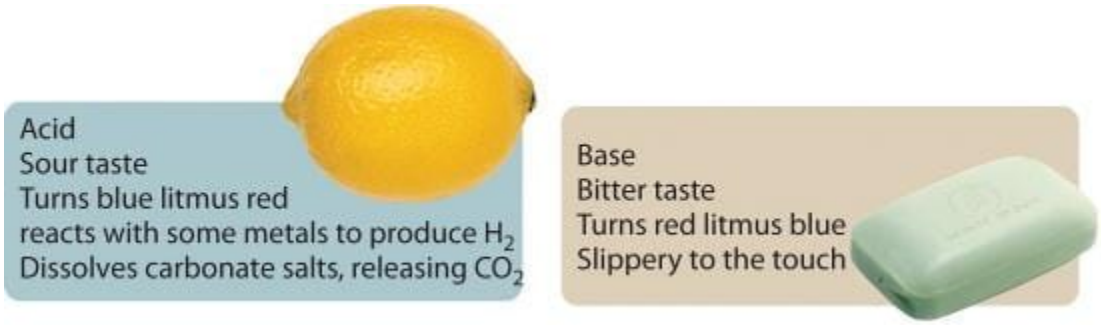
Learning Objectives

- To know the characteristic properties of acids and bases.

Acid–base reactions are essential in both biochemistry and industrial chemistry. Moreover, many of the substances we encounter in our homes, the supermarket, and the pharmacy are acids or bases. For example, aspirin is an acid (acetylsalicylic acid), and antacids are bases. In fact, every amateur chef who has prepared mayonnaise or squeezed a wedge of lemon to marinate a piece of fish has carried out an acid–base reaction. Before we discuss the characteristics of such reactions, let's first describe some of the properties of acids and bases.

Definitions of Acids and Bases

We can define **acids** as substances that dissolve in water to produce H^+ ions, whereas **bases** are defined as substances that dissolve in water to produce OH^- ions. In fact, this is only one possible set of definitions. Although the general properties of acids and bases have been known for more than a thousand years, the definitions of *acid* and *base* have changed dramatically as scientists have learned more about them. In ancient times, an acid was any substance that had a sour taste (e.g., vinegar or lemon juice), caused consistent color changes in dyes derived from plants (e.g., turning blue litmus paper red), reacted with certain metals to produce hydrogen gas and a solution of a salt containing a metal cation, and dissolved carbonate salts such as limestone ($CaCO_3$) with the evolution of carbon dioxide. In contrast, a base was any substance that had a bitter taste, felt slippery to the touch, and caused color changes in plant dyes that differed diametrically from the changes caused by acids (e.g., turning red litmus paper blue). Although these definitions were useful, they were entirely descriptive.



The Arrhenius Definition of Acids and Bases

The first person to define acids and bases in detail was the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry, 1903). According to the *Arrhenius definition*, an acid is a substance like hydrochloric acid that dissolves in water to produce H^+ ions (protons; Equation 4.3.1), and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide (OH^-) ions (Equation 4.3.2):

$$\underset{an\ Arrhenius\ acid}{HCl_{(g)}} \xrightarrow{H_2O_{(l)}} H^+_{(aq)} + Cl^-_{(aq)} \tag{4.3.1}$$

$$\underset{an\ Arrhenius\ base}{NaOH_{(s)}} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + OH^-_{(aq)} \tag{4.3.2}$$

According to Arrhenius, the characteristic properties of acids and bases are due exclusively to the presence of H^+ and OH^- ions, respectively, in solution. Although Arrhenius's ideas were widely accepted, his definition of acids and bases had two major limitations:

1. First, because acids and bases were defined in terms of ions obtained from water, the Arrhenius concept applied only to substances in aqueous solution.
2. Second, and more important, the Arrhenius definition predicted that *only* substances that dissolve in water to produce H^+ and OH^- ions should exhibit the properties of acids and bases, respectively. For example, according to the Arrhenius definition, the reaction of ammonia (a base) with gaseous HCl (an acid) to give ammonium chloride (Equation 4.3.3) is not an acid–base reaction because it does not involve H^+ and OH^-:

$$NH_{3\ (g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)} \tag{4.3.3}$$

The Brønsted–Lowry Definition of Acids and Bases

Because of the limitations of the Arrhenius definition, a more general definition of acids and bases was needed. One was proposed independently in 1923 by the Danish chemist J. N. Brønsted (1879–1947) and the British chemist T. M. Lowry (1874–1936), who defined acid–base reactions in terms of the transfer of a proton (H^+ ion) from one substance to another.

According to Brønsted and Lowry, an acid (A substance with at least one hydrogen atom that can dissociate to form an anion and an H^+ ion (a proton) in aqueous solution, thereby forming an acidic solution) is any substance that can donate a proton, and a base (a substance that produces one or more hydroxide ions (OH^- and a cation when dissolved in aqueous solution, thereby forming a basic solution) is any substance that can accept a proton. The Brønsted–Lowry definition of an acid is essentially the same as the Arrhenius definition, except that it is not restricted to aqueous solutions. The Brønsted–Lowry definition of a base, however, is far more general because the hydroxide ion is just one of many substances that can accept a proton. Ammonia, for example, reacts with a proton to form NH_4^+, so in Equation 4.3.3, NH_3 is a Brønsted–Lowry base and HCl is a Brønsted–Lowry acid. Because of its more general nature, the Brønsted–Lowry definition is used throughout this text unless otherwise specified.

Polyprotic Acids

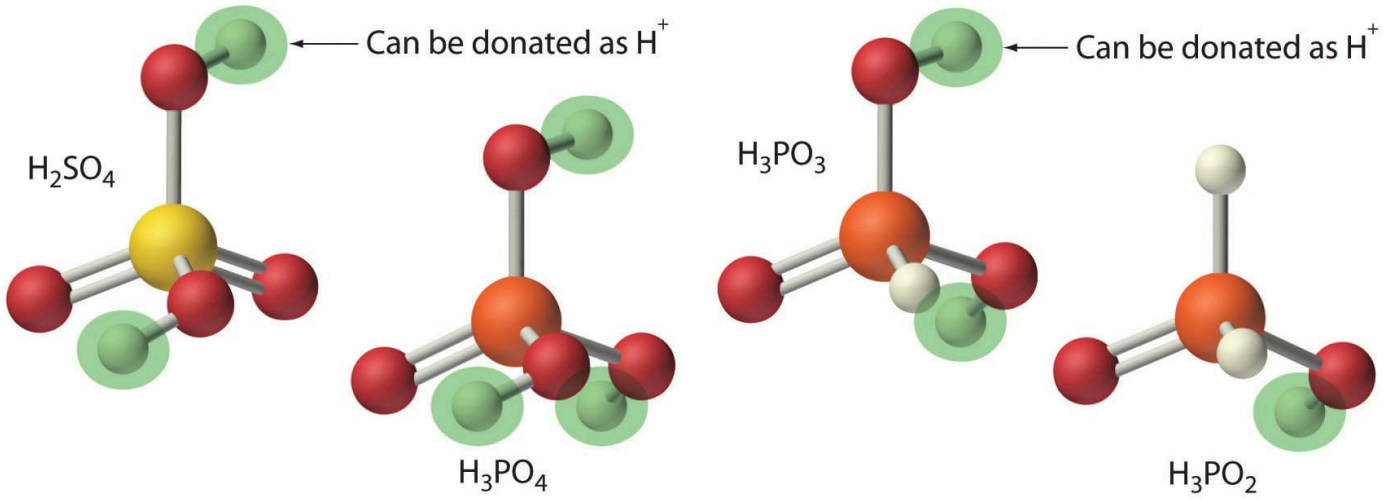
Acids differ in the number of protons they can donate. For example, monoprotic acids (a compound that is capable of donating one proton per molecule) are compounds that are capable of donating a single proton per molecule. Monoprotic acids include HF, HCl, HBr, HI, HNO_3, and HNO_2. All carboxylic acids that contain a single $–CO_2H$ group, such as acetic acid (CH_3CO_2H), are monoprotic acids, dissociating to form RCO_2^- and H^+. A compound that can donate more than one proton per molecule is known as a **polyprotic acid**. For example, H_2SO_4 can donate two H^+ ions in separate steps, so it is a diprotic acid (a compound that can donate two protons per molecule in separate steps) and H_3PO_4, which is capable of donating three protons in successive steps, is a triprotic acid (a compound that can donate three protons per molecule in separate steps), (Equation 4.3.4, Equation 4.3.5, and Equation 4.3.6):

$$H_3PO_4(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + H_2PO_4^-(aq) \tag{4.3.4}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \tag{4.3.5}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \tag{4.3.6}$$

In chemical equations such as these, a double arrow is used to indicate that both the forward and reverse reactions occur simultaneously, so the forward reaction does not go to completion. Instead, the solution contains significant amounts of both reactants and products. Over time, the reaction reaches a state in which the concentration of each species in solution remains constant. The reaction is then said to be in **equilibrium** (the point at which the rates of the forward and reverse reactions become the same, so that the net composition of the system no longer changes with time).



Ball and stick diagram of sulfuric acid, phosporic acid, phosphorous acid, and hypophosphorous acid with all of the hydrogen atoms highlighted to show availability to be donated as H positive ion.

Strengths of Acids and Bases

We will not discuss the strengths of acids and bases quantitatively until next semester. Qualitatively, however, we can state that **strong acids** react essentially completely with water to give H^+ and the corresponding anion. Similarly, **strong bases** dissociate essentially completely in water to give OH^- and the corresponding cation. Strong acids and strong bases are both strong electrolytes. In contrast, only a fraction of the molecules of weak acids and weak bases react with water to produce ions, so weak acids and weak bases are also weak electrolytes. Typically less than 5% of a weak electrolyte dissociates into ions in solution, whereas more than 95% is present in undissociated form.

In practice, only a few strong acids are commonly encountered: HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4 (H_3PO_4 is only moderately strong). The most common strong bases are ionic compounds that contain the hydroxide ion as the anion; three examples are NaOH, KOH, and $Ca(OH)_2$. Common weak acids include HCN, H_2S, HF, oxoacids such as HNO_2 and HClO, and carboxylic acids such as acetic acid. The ionization reaction of acetic acid is as follows:

$$CH_3CO_2H(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + CH_3CO_2^-(aq) \tag{4.3.7}$$

Although acetic acid is *very* soluble in water, almost all of the acetic acid in solution exists in the form of neutral molecules (less than 1% dissociates). Sulfuric acid is unusual in that it is a strong acid when it donates its first proton (Equation 4.3.8) but a weak acid when it donates its second proton (Equation 4.3.9) as indicated by the single and double arrows, respectively:

$$\underset{strong\ acid}{H_2SO_4(l)} \xrightarrow{H_2O(l)} H^+(aq) + HSO_4^-(aq) \tag{4.3.8}$$

$$\underset{weak\ acid}{HSO_4^-(aq)} \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \tag{4.3.9}$$

Consequently, an aqueous solution of sulfuric acid contains $H^+_{(aq)}$ ions and a mixture of $HSO^-_{4\ (aq)}$ and $SO^{2-}_{4\ (aq)}$ ions, but no H_2SO_4 molecules. All other polyprotic acids, such as H_3PO_4, are weak acids.

The most common weak base is ammonia, which reacts with water to form small amounts of hydroxide ion:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{4.3.10}$$

Most of the ammonia (>99%) is present in the form of NH_3(g). Amines, which are organic analogues of ammonia, are also weak bases, as are ionic compounds that contain anions derived from weak acids (such as S^{2-}).

> There is no correlation between the solubility of a substance and whether it is a strong electrolyte, a weak electrolyte, or a nonelectrolyte.

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Definition of Strong/Weak Acids & Bases: Definition of Strong/Weak Acids & Bases, YouTube (opens in new window) [Definition of Strong] [Definition of Strong] [youtu.be] (opens in new window)

Table 4.3.1 lists some common strong acids and bases. Acids other than the six common strong acids are almost invariably weak acids. The only common strong bases are the hydroxides of the alkali metals and the heavier alkaline earths (Ca, Sr, and Ba); any other bases you encounter are most likely weak. Remember that *there is no correlation between solubility and whether a substance is a strong or a weak electrolyte!* Many weak acids and bases are extremely soluble in water.

Table 4.3.1: Common Strong Acids and Bases

Strong Acids		Strong Bases	
Hydrogen Halides	**Oxoacids**	**Group 1 Hydroxides**	**Hydroxides of Heavy Group 2 Elements**
HCl	HNO_3	LiOH	$Ca(OH)_2$
HBr	H_2SO_4	NaOH	$Sr(OH)_2$
HI	$HClO_4$	KOH	$Ba(OH)_2$
		RbOH	
		CsOH	

Example 4.3.1: Acid Strength

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

a. $CH_3CH_2CO_2H$
b. CH_3OH
c. $Sr(OH)_2$
d. $CH_3CH_2NH_2$
e. $HBrO_4$

Given: compound

Asked for: acid or base strength

Strategy:

A Determine whether the compound is organic or inorganic.

B If inorganic, determine whether the compound is acidic or basic by the presence of dissociable H^+ or OH^- ions, respectively. If organic, identify the compound as a weak base or a weak acid by the presence of an amine or a carboxylic acid group, respectively. Recall that all polyprotic acids except H_2SO_4 are weak acids.

Solution:

a. **A** This compound is propionic acid, which is organic. **B** It contains a carboxylic acid group analogous to that in acetic acid, so it must be a weak acid.
b. **A** CH_3OH is methanol, an organic compound that contains the –OH group. **B** As a covalent compound, it does not dissociate to form the OH^- ion. Because it does not contain a carboxylic acid ($–CO_2H$) group, methanol also cannot dissociate to form $H^+(aq)$ ions. Thus we predict that in aqueous solution methanol is neither an acid nor a base.
c. **A** $Sr(OH)_2$ is an inorganic compound that contains one Sr^{2+} and two OH^- ions per formula unit. **B** We therefore expect it to be a strong base, similar to $Ca(OH)_2$.
d. **A** $CH_3CH_2NH_2$ is an amine (ethylamine), an organic compound in which one hydrogen of ammonia has been replaced by an R group. **B** Consequently, we expect it to behave similarly to ammonia (Equation 4.3.7), reacting with water to produce small amounts of the OH^- ion. Ethylamine is therefore a weak base.
e. **A** $HBrO_4$ is perbromic acid, an inorganic compound. **B** It is not listed in Table 4.3.1 as one of the common strong acids, but that does not necessarily mean that it is a weak acid. If you examine the periodic table, you can see that Br lies directly below Cl in group 17. We might therefore expect that $HBrO_4$ is chemically similar to $HClO_4$, a strong acid—and, in fact, it is.

Exercise 4.3.1: Acid Strength

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

a. $Ba(OH)_2$
b. HIO_4
c. $CH_3CH_2CH_2CO_2H$
d. $(CH_3)_2NH$
e. CH_2O

Answer a available at the end of this section.

Answers

Exercise 4.3.1: Acid Strength

strong base
strong acid
weak acid
weak base
none of these; formaldehyde is a neutral molecule

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4.4: Oxidation-Reduction Reactions

Learning Objectives

- To identify oxidation–reduction reactions in solution.

The term oxidation was first used to describe reactions in which metals react with oxygen in air to produce metal oxides. When iron is exposed to air in the presence of water, for example, the iron turns to rust—an iron oxide. When exposed to air, aluminum metal develops a continuous, transparent layer of aluminum oxide on its surface. In both cases, the metal acquires a positive charge by transferring electrons to the neutral oxygen atoms of an oxygen molecule. As a result, the oxygen atoms acquire a negative charge and form oxide ions (O^{2-}). Because the metals have lost electrons to oxygen, they have been oxidized; oxidation is therefore the loss of electrons. Conversely, because the oxygen atoms have gained electrons, they have been reduced, so reduction is the gain of electrons. For every oxidation, there must be an associated reduction. Therefore, these reactions are known as oxidation-reduction reactions, or "redox" reactions for short.

> Any oxidation must ALWAYS be accompanied by a reduction and vice versa.

Originally, the term reduction referred to the decrease in mass observed when a metal oxide was heated with carbon monoxide, a reaction that was widely used to extract metals from their ores. When solid copper(I) oxide is heated with hydrogen, for example, its mass decreases because the formation of pure copper is accompanied by the loss of oxygen atoms as a volatile product (water vapor). The reaction is as follows:

$$\mathrm{Cu_2O\,(s) + H_2\,(g)\ \rightarrow 2\,Cu\,(s) + H_2O\,(g)} \tag{4.4.1}$$

Oxidation-reduction reactions are now defined as reactions that exhibit a change in the oxidation states of one or more elements in the reactants by a transfer of electrons, which follows the mnemonic "oxidation is loss, reduction is gain", or **"oil rig"**. The **oxidation state** of each atom in a compound is the charge an atom would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons. Atoms in their elemental form, such as O_2 or H_2, are assigned an oxidation state of zero. For example, the reaction of aluminum with oxygen to produce aluminum oxide is

$$\mathrm{4\,Al\,(s) + 3\,O_2\ \rightarrow 2\,Al_2O_3\,(s)} \tag{4.4.2}$$

Each neutral oxygen atom gains two electrons and becomes negatively charged, forming an oxide ion; thus, oxygen has an oxidation state of –2 in the product and has been reduced. Each neutral aluminum atom loses three electrons to produce an aluminum ion with an oxidation state of +3 in the product, so aluminum has been oxidized. In the formation of Al_2O_3, electrons are transferred as follows (the small overset number emphasizes the oxidation state of the elements):

$$\mathrm{\overset{0}{4Al} + 3\overset{0}{O_2} \rightarrow 4\,Al^{3+} + 6\,O^{2-}} \tag{4.4.3}$$

Equation 4.4.1 and Equation 4.4.2 are examples of oxidation–reduction (redox) reactions. In redox reactions, there is a net transfer of electrons from one reactant to another. In any redox reaction, the total number of electrons lost must equal the total of electrons gained to preserve electrical neutrality. In Equation 4.4.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$\begin{aligned}\text{electrons lost} &= 4\,\text{Al atoms} \times \frac{3\,e^-\,\text{lost}}{\text{Al atom}} \\ &= 12\,e^-\,\text{lost}\end{aligned}$$

$$\begin{aligned}\text{electrons gained} &= 6\,\text{O atoms} \times \frac{2\,e^-\,\text{gained}}{\text{O atom}} \\ &= 12\,e^-\,\text{gained}\end{aligned}$$

The same pattern is seen in all oxidation–reduction reactions: the number of electrons lost must equal the number of electrons gained. An additional example of a redox reaction, the reaction of sodium metal with chlorine is illustrated in Figure 4.4.1.

In all oxidation–reduction (redox) reactions, the number of electrons lost equals the number of electrons gained.

Assigning Oxidation States

Assigning oxidation states to the elements in binary ionic compounds is straightforward: the oxidation states of the elements are identical to the charges on the monatomic ions. Previously, you learned how to predict the formulas of simple ionic compounds based on the sign and magnitude of the charge on monatomic ions formed by the neutral elements. Examples of such compounds are sodium chloride (NaCl; Figure 4.4.1), magnesium oxide (MgO), and calcium chloride ($CaCl_2$). In covalent compounds, in contrast, atoms share electrons. However, we can still assign oxidation states to the elements involved by treating them as if they were ionic (that is, as if all the bonding electrons were transferred to the more attractive element). Oxidation states in covalent compounds are somewhat arbitrary, but they are useful bookkeeping devices to help you understand and predict many reactions.

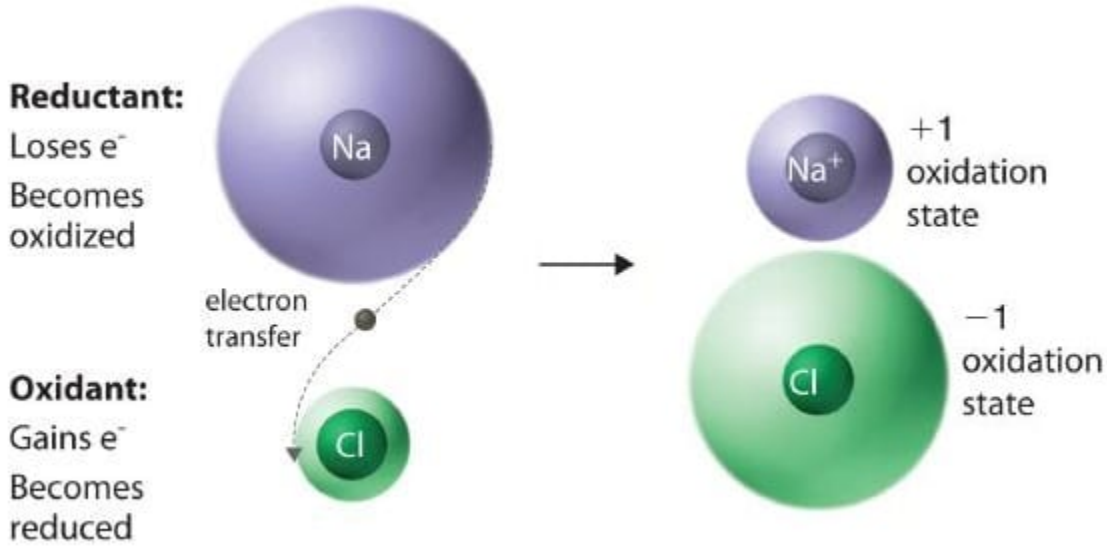


Figure 4.4.1: The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom. The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.

Sodium atom acts as the reductant and chlorine as the oxidant. The result is an oxidation state of positive 1 and negative 1 for sodium and chloride ion respectively.

A set of rules for assigning oxidation states to atoms in chemical compounds follows.

Rules for Assigning Oxidation States

1. The oxidation state of an atom in any pure element, whether monatomic, diatomic, or polyatomic, is zero.
2. The oxidation state of a monatomic ion is the same as its charge—for example, $Na^+ = +1$, $Cl^- = -1$.
3. The oxidation state of fluorine in chemical compounds is always –1. Other halogens usually have oxidation states of –1 as well, except when combined with oxygen or other halogens.
4. Hydrogen is assigned an oxidation state of +1 in its compounds with nonmetals and –1 in its compounds with metals.
5. Oxygen is normally assigned an oxidation state of –2 in compounds, with two exceptions: in compounds that contain oxygen–fluorine or oxygen–oxygen bonds, the oxidation state of oxygen is determined by the oxidation states of the other elements present.
6. The sum of the oxidation states of all the atoms in a neutral molecule or ion must equal the charge on the molecule or ion.

Nonintegral (fractional) oxidation states are encountered occasionally. They are usually due to the presence of two or more atoms of the same element with different oxidation states.

In any chemical reaction, the net charge must be conserved; that is, in a chemical reaction, the total number of electrons is constant, just like the total number of atoms. Consistent with this, rule 1 states that the sum of the individual oxidation states of

the atoms in a molecule or ion must equal the net charge on that molecule or ion. In NaCl, for example, Na has an oxidation state of +1 and Cl is –1. The net charge is zero, as it must be for any compound.

Rule 3 is required because fluorine attracts electrons more strongly than any other element, for reasons you will discover in Chapter 6. Hence fluorine provides a reference for calculating the oxidation states of other atoms in chemical compounds. Rule 4 reflects the difference in chemistry observed for compounds of hydrogen with nonmetals (such as chlorine) as opposed to compounds of hydrogen with metals (such as sodium). For example, NaH contains the H^- ion, whereas HCl forms H^+ and Cl^- ions when dissolved in water. Rule 5 is necessary because fluorine has a greater attraction for electrons than oxygen does; this rule also prevents violations of rule 2. So the oxidation state of oxygen is +2 in OF_2 but –½ in KO_2. Note that an oxidation state of –½ for O in KO_2 is perfectly acceptable.

The reduction of copper(I) oxide shown in Equation 4.4.4 demonstrates how to apply these rules. Rule 1 states that atoms in their elemental form have an oxidation state of zero, which applies to H_2 and Cu. From rule 4, hydrogen in H_2O has an oxidation state of +1, and from rule 5, oxygen in both Cu_2O and H_2O has an oxidation state of –2. Rule 6 states that the sum of the oxidation states in a molecule or formula unit must equal the net charge on that compound. This means that each Cu atom in Cu_2O must have a charge of +1: 2(+1) + (–2) = 0. So the oxidation states are as follows:

$$\overset{+1}{\mathrm{Cu}}_2\overset{-2}{\mathrm{O}}(s) + \overset{0}{\mathrm{H}}_2(g) \rightarrow 2\overset{0}{\mathrm{Cu}}(s) + \overset{+1}{\mathrm{H}}_2\overset{-2}{\mathrm{O}}(g) \tag{4.4.4}$$

Assigning oxidation states allows us to see that there has been a net transfer of electrons from hydrogen (0 → +1) to copper (+1 → 0). Thus, this is a redox reaction. Once again, the number of electrons lost equals the number of electrons gained, and there is a net conservation of charge:

$$\text{electrons lost} = 2\,H\,\text{atoms} \times \frac{1\,e^-\,\text{lost}}{H\,\text{atom}} = 2\,e^-\,\text{lost} \tag{4.4.5}$$

$$\text{electrons gained} = 2\,Cu\,\text{atoms} \times \frac{1\,e^-\,\text{gained}}{Cu\,\text{atom}} = 2\,e^-\,\text{gained} \tag{4.4.6}$$

Remember that oxidation states are useful for visualizing the transfer of electrons in oxidation–reduction reactions, but the oxidation state of an atom and its actual charge are the same only for simple ionic compounds. Oxidation states are a convenient way of assigning electrons to atoms, and they are useful for predicting the types of reactions that substances undergo.

Example 4.4.1: Oxidation States

Assign oxidation states to all atoms in each compound.

a. sulfur hexafluoride (SF_6)
b. methanol (CH_3OH)
c. ammonium sulfate [$(NH_4)2SO_4$]
d. magnetite (Fe_3O_4)
e. ethanoic (acetic) acid (CH_3CO_2H)

Given: molecular or empirical formula

Asked for: oxidation states

Strategy:

Begin with atoms whose oxidation states can be determined unambiguously from the rules presented (such as fluorine, other halogens, oxygen, and monatomic ions). Then determine the oxidation states of other atoms present according to rule 1.

Solution:

a. We know from rule 3 that fluorine always has an oxidation state of –1 in its compounds. The six fluorine atoms in sulfur hexafluoride give a total negative charge of –6. Because rule 1 requires that the sum of the oxidation states of all atoms be zero in a neutral molecule (here SF_6), the oxidation state of sulfur must be +6:

[(6 F atoms)(−1)] + [(1 S atom) (+6)] = 0

b. According to rules 4 and 5, hydrogen and oxygen have oxidation states of +1 and −2, respectively. Because methanol has no net charge, carbon must have an oxidation state of −2:

[(4 H atoms)(+1)] + [(1 O atom)(−2)] + [(1 C atom)(−2)] = 0

c. Note that $(NH_4)_2SO_4$ is an ionic compound that consists of both a polyatomic cation (NH_4^+) and a polyatomic anion (SO_4^{2-}) (see Table 2.4). We assign oxidation states to the atoms in each polyatomic ion separately. For NH_4^+, hydrogen has an oxidation state of +1 (rule 4), so nitrogen must have an oxidation state of −3:

[(4 H atoms)(+1)] + [(1 N atom)(−3)] = +1, the charge on the NH_4^+ ion

For SO42−, oxygen has an oxidation state of −2 (rule 5), so sulfur must have an oxidation state of +6:

[(4 O atoms) (−2)] + [(1 S atom)(+6)] = −2, the charge on the sulfate ion

d. Oxygen has an oxidation state of −2 (rule 5), giving an overall charge of −8 per formula unit. This must be balanced by the positive charge on three iron atoms, giving an oxidation state of +8/3 for iron:

[(4 O atoms)(−2)]+[(3 Fe atoms)$\left(+\frac{8}{3}\right)$]= 0

Fractional oxidation states are allowed because oxidation states are a somewhat arbitrary way of keeping track of electrons. In fact, Fe_3O_4 can be viewed as having two Fe^{3+} ions and one Fe^{2+} ion per formula unit, giving a net positive charge of +8 per formula unit. Fe_3O_4 is a magnetic iron ore commonly called magnetite. In ancient times, magnetite was known as lodestone because it could be used to make primitive compasses that pointed toward Polaris (the North Star), which was called the “lodestar.”

e. Initially, we assign oxidation states to the components of CH_3CO_2H in the same way as any other compound. Hydrogen and oxygen have oxidation states of +1 and −2 (rules 4 and 5, respectively), resulting in a total charge for hydrogen and oxygen of

[(4 H atoms)(+1)] + [(2 O atoms)(−2)] = 0

So the oxidation state of carbon must also be zero (rule 6). This is, however, an average oxidation state for the two carbon atoms present. Because each carbon atom has a different set of atoms bonded to it, they are likely to have different oxidation states. To determine the oxidation states of the individual carbon atoms, we use the same rules as before but with the additional assumption that bonds between atoms of the same element do not affect the oxidation states of those atoms. The carbon atom of the methyl group ($-CH_3$) is bonded to three hydrogen atoms and one carbon atom. We know from rule 4 that hydrogen has an oxidation state of +1, and we have just said that the carbon–carbon bond can be ignored in calculating the oxidation state of the carbon atom. For the methyl group to be electrically neutral, its carbon atom must have an oxidation state of −3. Similarly, the carbon atom of the carboxylic acid group ($-CO_2H$) is bonded to one carbon atom and two oxygen atoms. Again ignoring the bonded carbon atom, we assign oxidation states of −2 and +1 to the oxygen and hydrogen atoms, respectively, leading to a net charge of

[(2 O atoms)(−2)] + [(1 H atom)(+1)] = −3

To obtain an electrically neutral carboxylic acid group, the charge on this carbon must be +3. The oxidation states of the individual atoms in acetic acid are thus

$$\overset{-3}{C}\overset{+1}{H_3}\overset{+3}{C}\overset{-2}{O_2}\overset{+1}{H}$$

Thus the sum of the oxidation states of the two carbon atoms is indeed zero.

Exercise 4.4.1: Oxidation States

Assign oxidation states to all atoms in each compound.

a. barium fluoride (BaF_2)
b. formaldehyde (CH_2O)
c. potassium dichromate ($K_2Cr_2O_7$)
d. cesium oxide (CsO_2)
e. ethanol (CH_3CH_2OH)

Answer a available at the end of this section.

Types of Redox Reactions

Many types of chemical reactions are classified as redox reactions, and it would be impossible to memorize all of them. However, there are a few important types of redox reactions that you are likely to encounter and should be familiar with. These include:

- **Synthesis** reactions: The formation of any compound directly from the elements is a redox reaction, for example, the formation of water from hydrogen and oxygen:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$

- **Decomposition** reactions: Conversely, the decomposition of a compound to its elements is also a redox reaction, as in the electrolysis of water:

$$2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2\,(g)$$

- **Combustion** reactions: Many chemicals combust (burn) with oxygen. In particular, organic chemicals such as hydrocarbons burn in the presence of oxygen to produce carbon dioxide and water as the products:

$$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

The following sections describe another important class of redox reactions: single-displacement reactions of metals in solution.

Redox Reactions of Solid Metals in Aqueous Solution

- A widely encountered class of oxidation–reduction reactions is the reaction of aqueous solutions of acids or metal salts with solid metals. An example is the corrosion of metal objects, such as the rusting of an automobile (Figure 4.4.2). Rust is formed from a complex oxidation–reduction reaction involving dilute acid solutions that contain Cl^- ions (effectively, dilute HCl), iron metal, and oxygen. When an object rusts, iron metal reacts with HCl(aq) to produce iron(II) chloride and hydrogen gas:

$$Fe\,(s) + 2\,HCl\,(aq) \rightarrow FeCl_2\,(aq) + H_2\,(g) \tag{4.4.7}$$

  In subsequent steps, $FeCl_2$ undergoes oxidation to form a reddish-brown precipitate of $Fe(OH)_3$.



Figure 4.4.2: Rust Formation. The corrosion process involves an oxidation–reduction reaction in which metallic iron is converted to $Fe(OH)_3$, a reddish-brown solid.

Many metals dissolve through reactions of this type, which have the general form

$$\text{metal} + \text{acid} \rightarrow \text{salt} + \text{hydrogen} \tag{4.4.8}$$

Some of these reactions have important consequences. For example, it has been proposed that one factor that contributed to the fall of the Roman Empire was the widespread use of lead in cooking utensils and pipes that carried water. Rainwater, as we have seen, is slightly acidic, and foods such as fruits, wine, and vinegar contain organic acids. In the presence of these acids, lead dissolves:

$$\mathrm{Pb\,(s) + 2\,H^+\,(aq)\ \rightarrow Pb^{2+}\,(aq) + H_2\,(g)} \tag{4.4.9}$$

Consequently, it has been speculated that both the water and the food consumed by Romans contained toxic levels of lead, which resulted in widespread lead poisoning and eventual madness. Perhaps this explains why the Roman Emperor Caligula appointed his favorite horse as consul!

• Single-Displacement Reactions

Certain metals are oxidized by aqueous acid, whereas others are oxidized by aqueous solutions of various metal salts. Both types of reactions are called single-displacement reactions, in which the ion in solution is displaced through oxidation of the metal. Two examples of single-displacement reactions are the reduction of iron salts by zinc (Equation 4.4.10) and the reduction of silver salts by copper (Equation 4.4.11 and Figure 4.4.3):

$$\mathrm{Zn\,(s) + Fe^{2+}\,(aq)\ \rightarrow Zn^{2+}\,(aq) + Fe\,(s)} \tag{4.4.10}$$

$$\mathrm{Cu\,(s) + 2\,Ag^+\,(aq)\ \rightarrow Cu^{2+}\,(aq) + 2\,Ag\,(s)} \tag{4.4.11}$$

The reaction in Equation 4.4.10 is widely used to prevent (or at least postpone) the corrosion of iron or steel objects, such as nails and sheet metal. The process of “galvanizing” consists of applying a thin coating of zinc to the iron or steel, thus protecting it from oxidation as long as zinc remains on the object.



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The Activity Series

By observing what happens when samples of various metals are placed in contact with solutions of other metals, chemists have arranged the metals according to the relative ease or difficulty with which they can be oxidized in a single-displacement reaction. For example, metallic zinc reacts with iron salts, and metallic copper reacts with silver salts. Experimentally, it is found that zinc reacts with both copper salts and silver salts, producing $\mathrm{Zn_2}^{+}$. Zinc therefore has a greater tendency to be oxidized than does iron, copper, or silver. Although zinc will not react with magnesium salts to give magnesium metal, magnesium metal will react with zinc salts to give zinc metal:

$$\mathrm{Zn\,(s) + Mg^{2+}\,(aq)} \not\rightarrow \mathrm{Zn^{2+}\,(aq) + Mg\,(s)} \tag{4.4.12}$$

$$\mathrm{Mg\,(s) + Zn^{2+}\,(aq)} \rightarrow \mathrm{Mg^{2+}\,(aq) + Zn\,(s)} \tag{4.4.13}$$

Magnesium has a greater tendency to be oxidized than zinc does.

Pairwise reactions of this sort are the basis of the activity series (Figure $4.4.4$), which lists metals and hydrogen in order of their relative tendency to be oxidized. The metals at the top of the series, which have the greatest tendency to lose electrons, are the alkali metals (group 1), the alkaline earth metals (group 2), and Al (group 13). In contrast, the metals at the bottom of the series, which have the lowest tendency to be oxidized, are the precious metals or coinage metals—platinum, gold, silver, and copper, and mercury, which are located in the lower right portion of the metals in the periodic table. You should be generally familiar with which kinds of metals are active metals, which have the greatest tendency to be oxidized. (located at the top of the series) and which are inert metals, which have the least tendency to be oxidized. (at the bottom of the series).

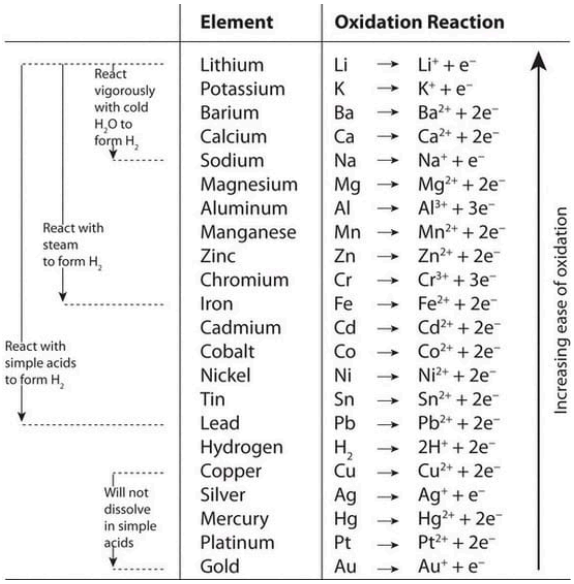


Figure 4.4.4: The Activity Series

When using the activity series to predict the outcome of a reaction, keep in mind that *any element will reduce compounds of the elements below it in the series*. Because magnesium is above zinc in Figure 4.4.4, magnesium metal will reduce zinc salts but not vice versa. Similarly, the precious metals are at the bottom of the activity series, so virtually any other metal will reduce precious metal salts to the pure precious metals. Hydrogen is included in the series, and the tendency of a metal to react with an acid is indicated by its position relative to hydrogen in the activity series. *Only those metals that lie above hydrogen in the activity series dissolve in acids to produce H_2*. Because the precious metals lie below hydrogen, they do not dissolve in dilute acid and therefore do not corrode readily. Example 4.4.2 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions.

Example 4.4.2: Activity

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

a. A strip of aluminum foil is placed in an aqueous solution of silver nitrate.
b. A few drops of liquid mercury are added to an aqueous solution of lead(II) acetate.
c. Some sulfuric acid from a car battery is accidentally spilled on the lead cable terminals.

Given: reactants

Asked for: overall reaction and net ionic equation

Strategy:

A. Locate the reactants in the activity series in Figure 4.4.4 and from their relative positions, predict whether a reaction will occur. If a reaction does occur, identify which metal is oxidized and which is reduced.
B. Write the net ionic equation for the redox reaction.

Solution:

1. **A** Aluminum is an active metal that lies above silver in the activity series, so we expect a reaction to occur. According to their relative positions, aluminum will be oxidized and dissolve, and silver ions will be reduced to silver metal. **B** The net ionic equation is as follows:

$$\mathrm{Al(s) + 3\,Ag^+(aq) \rightarrow Al^{3+}(aq) + 3\,Ag(s)}$$

Recall from our discussion of solubilities that most nitrate salts are soluble. In this case, the nitrate ions are spectator ions and are not involved in the reaction.

2. **A** Mercury lies below lead in the activity series, so no reaction will occur.
3. **A** Lead is above hydrogen in the activity series, so the lead terminals will be oxidized, and the acid will be reduced to form H_2. **B** From our discussion of solubilities, recall that Pb^{2+} and $SO_4{}^{2-}$ form insoluble lead(II) sulfate. In this case, the sulfate ions are *not* spectator ions, and the reaction is as follows:

$$\mathrm{Pb\,(s) + 2\,H^+\,(aq) + SO_4{}^{2-}\,(aq) \rightarrow PbSO_4\,(s) + H_2\,(g)}$$

Lead(II) sulfate is the white solid that forms on corroded battery terminals.



Corroded battery terminals. *The white solid is lead(II) sulfate, formed from the reaction of solid lead with a solution of sulfuric acid.*

Exercise 4.4.2

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

a. A strip of chromium metal is placed in an aqueous solution of aluminum chloride.
b. A strip of zinc is placed in an aqueous solution of chromium(III) nitrate.
c. A piece of aluminum foil is dropped into a glass that contains vinegar (the active ingredient is acetic acid).

Answer a available at the end of this section.

Summary

Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation. In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation–reduction reactions in solution using the **oxidation state method** (Table 4.4.1), in which the overall reaction is separated into an oxidation equation and a reduction equation. There are many types of redox reactions. **Single-displacement reactions** are reactions of metals with either acids or another metal salt that result in dissolution of the first metal and precipitation of a second (or evolution of hydrogen gas). The outcome of these reactions can be predicted using the **activity series** (Figure 4.4.4), which arranges metals and H_2 in decreasing order of their tendency to be oxidized. Any metal will reduce metal ions below it in the activity series. **Active metals** lie at the top of the activity series, whereas **inert metals** are at the bottom of the activity series.

Answers

Exercise $4.4.1$**: Oxidation States**

Ba, +2; F, −1

C, 0; H, +1; O, −2

K, +1; Cr, +6; O, −2

Cs, +1; O, −½

C, −3; H, +1; C, −1; H, +1; O, −2; H, +1

Exercise $4.4.2$

$no\ reaction$

$3Zn(s) + 2Cr^{3+}(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr(s)$

\(2Al(s) + 6CH_3CO_2H(aq) \rightarrow 2Al^{3+}(aq) + 6CH_3CO_2^-(aq) + 3H_2(g)\

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4.5: Concentration of Solutions

Learning Objectives

- To describe the concentrations of solutions quantitatively

Many people have a qualitative idea of what is meant by *concentration*. Anyone who has made instant coffee or lemonade knows that too much powder gives a strongly flavored, highly concentrated drink, whereas too little results in a dilute solution that may be hard to distinguish from water. In chemistry, the concentration of a solution is the quantity of a **solute** that is contained in a particular quantity of **solvent** or solution. Knowing the concentration of solutes is important in controlling the stoichiometry of reactants for solution reactions. Chemists use many different methods to define concentrations, some of which are described in this section.

Molarity

The most common unit of concentration is *molarity*, which is also the most useful for calculations involving the stoichiometry of reactions in solution. The molarity (M) is defined as the number of moles of solute present in exactly 1 L of solution. It is, equivalently, the number of millimoles of solute present in exactly 1 mL of solution:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{4.5.1}$$

The units of molarity are therefore moles per liter of solution (mol/L), abbreviated as M. An aqueous solution that contains 1 mol (342 g) of sucrose in enough water to give a final volume of 1.00 L has a sucrose concentration of 1.00 mol/L or 1.00 M. In chemical notation, square brackets around the name or formula of the solute represent the molar concentration of a solute. Therefore,

$$[\text{sucrose}] = 1.00\ \text{M}$$

is read as “the concentration of sucrose is 1.00 molar.” The relationships between volume, molarity, and moles may be expressed as either

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{4.5.2}$$

or

$$V_{mL} M_{mmol/mL} = \cancel{mL}\left(\frac{mmol}{\cancel{mL}}\right) = mmoles \tag{4.5.3}$$

Figure 4.5.1 illustrates the use of Equations 4.5.2 and 4.5.3.



(a) An amount of solute is weighed out on an analytical balance and then

(b) A portion of the solvent is added to the volumetric flask.

(c) The mixture is swirled until *all* of the solute is dissolved.

(d) Additional solvent is added up to the mark on the volumetric flask.

Figure 4.5.1: Preparation of a Solution of Known Concentration Using a Solid Solute

Example 4.5.1: Calculating Moles from Concentration of NaOH

Calculate the number of moles of sodium hydroxide (NaOH) in 2.50 L of 0.100 M NaOH.

Given: identity of solute and volume and molarity of solution

Asked for: amount of solute in moles

Strategy:

Use either Equation 4.5.2 or Equation 4.5.3, depending on the units given in the problem.

Solution:

Because we are given the volume of the solution in liters and are asked for the number of moles of substance, Equation 4.5.2 is more useful:

$$moles\ \ NaOH = V_L M_{mol/L} = (2.50\ \cancel{L}) \left(\frac{0.100\ mol}{\cancel{L}} \right) = 0.250\ \ mol\ \ NaOH$$

Exercise 4.5.1: Calculating Moles from Concentration of Alanine

Calculate the number of millimoles of alanine, a biologically important molecule, in 27.2 mL of 1.53 M alanine.

Answer available at the end of this section.

YouTube Video

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Calculations Involving Molarity (M): Calculations Involving Molarity (M), YouTube(opens in new window) [youtu.be]

Concentrations are also often reported on a mass-to-mass (m/m) basis or on a mass-to-volume (m/v) basis, particularly in clinical laboratories and engineering applications. A concentration expressed on an m/m basis is equal to the number of grams of solute per gram of solution; a concentration on an m/v basis is the number of grams of solute per milliliter of solution. Each measurement can be expressed as a percentage by multiplying the ratio by 100; the result is reported as percent m/m or percent m/v. The concentrations of very dilute solutions are often expressed in *parts per million* (*ppm*), which is grams of solute per 10^6 g of solution, or in *parts per billion* (*ppb*), which is grams of solute per 10^9 g of solution. For aqueous solutions at 20°C, 1 ppm corresponds to 1 µg per milliliter, and 1 ppb corresponds to 1 ng per milliliter. These concentrations and their units are summarized in Table 4.5.1.

Table 4.5.1: Common Units of Concentration

Concentration	Units
m/m	g of solute/g of solution
m/v	g of solute/mL of solution
ppm	g of solute/10^6 g of solution
	µg/mL
ppb	g of solute/10^9 g of solution
	ng/mL

The Preparation of Solutions

To prepare a solution that contains a specified concentration of a substance, it is necessary to dissolve the desired number of moles of solute in enough solvent to give the desired final volume of solution. Figure 4.5.1 illustrates this procedure for a solution of cobalt(II) chloride dihydrate in ethanol. Note that the volume of the *solvent* is not specified. Because the solute occupies space in the solution, the volume of the solvent needed is almost always *less* than the desired volume of solution. For example, if the desired volume were 1.00 L, it would be incorrect to add 1.00 L of water to 342 g of sucrose because that would produce more than 1.00 L of solution. As shown in Figure 4.5.2, for some substances this effect can be significant, especially for concentrated solutions.

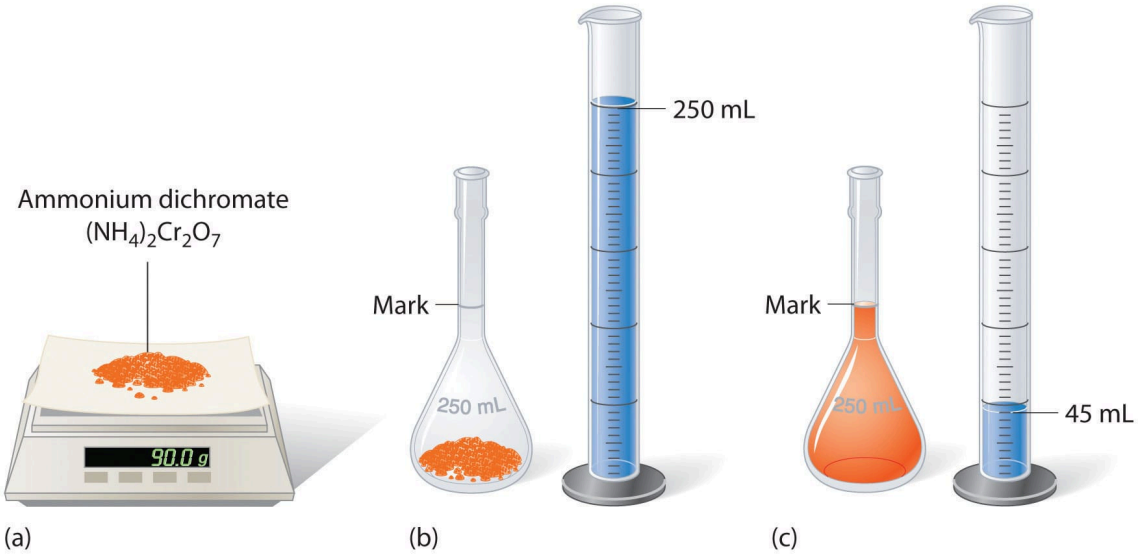


Figure 4.5.2: Preparation of 250 mL of a Solution of $(NH_4)_2Cr_2O_7$ in Water. The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.

45 milliliters of water remain in the graduated cylinder even after addition to the mark of the volumetric flask.

Example 4.5.2

The solution contains 10.0 g of cobalt(II) chloride dihydrate, $CoCl_2$•$2H_2O$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $\mathrm{CoCl_2 \cdot 2\,H_2O}$?

Given: mass of solute and volume of solution

Asked for: concentration (M)

Strategy:

To find the number of moles of $\mathrm{CoCl_2 \cdot 2\,H_2O}$, divide the mass of the compound by its molar mass. Calculate the molarity of the solution by dividing the number of moles of solute by the volume of the solution in liters.

Solution:

The molar mass of $CoCl_2$•$2H_2O$ is 165.87 g/mol. Therefore,

$$moles\ CoCl_2 \cdot 2H_2O = \left(\frac{10.0\ \cancel{g}}{165.87\ \cancel{g}/mol}\right) = 0.0603\ mol$$

The volume of the solution in liters is

$$volume = 500\ \cancel{mL}\left(\frac{1\ L}{1000\ \cancel{mL}}\right) = 0.500\ L$$

Molarity is the number of moles of solute per liter of solution, so the molarity of the solution is

$$molarity = \frac{0.0603\ mol}{0.500\ L} = 0.121\ M = CoCl_2 \cdot H_2O$$

Exercise 4.5.2

The solution shown in Figure 4.5.2 contains 90.0 g of $(NH_4)_2Cr_2O_7$ in enough water to give a final volume of exactly 250 mL. What is the molar concentration of ammonium dichromate?

Answer available at the end of this section.

To prepare a particular volume of a solution that contains a specified concentration of a solute, we first need to calculate the number of moles of solute in the desired volume of solution using the relationship shown in Equation 4.5.2. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example 4.5.3.

Example 4.5.3: D5W Solution

The so-called D5W solution used for the intravenous replacement of body fluids contains 0.310 M glucose. (D5W is an approximately 5% solution of dextrose [the medical name for glucose] in water.) Calculate the mass of glucose necessary to prepare a 500 mL pouch of D5W. Glucose has a molar mass of 180.16 g/mol.

Given: molarity, volume, and molar mass of solute

Asked for: mass of solute

Strategy:

A. Calculate the number of moles of glucose contained in the specified volume of solution by multiplying the volume of the solution by its molarity.
B. Obtain the mass of glucose needed by multiplying the number of moles of the compound by its molar mass.

Solution:

A We must first calculate the number of moles of glucose contained in 500 mL of a 0.310 M solution:

$$V_L M_{mol/L} = moles$$

$$500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.310\ mol\ glucose}{1\ \cancel{L}}\right) = 0.155\ \ mol\ \ glucose$$

B We then convert the number of moles of glucose to the required mass of glucose:

$$mass\ \ of\ \ glucose = 0.155\ \ \cancel{mol\ glucose}\left(\frac{180.16\ g\ glucose}{1\ \ \cancel{mol\ glucose}}\right) = 27.9\ \ g\ \ glucose$$

Exercise 4.5.3

Another solution commonly used for intravenous injections is normal saline, a 0.16 M solution of sodium chloride in water. Calculate the mass of sodium chloride needed to prepare 250 mL of normal saline solution.

Answer available at the end of this section.

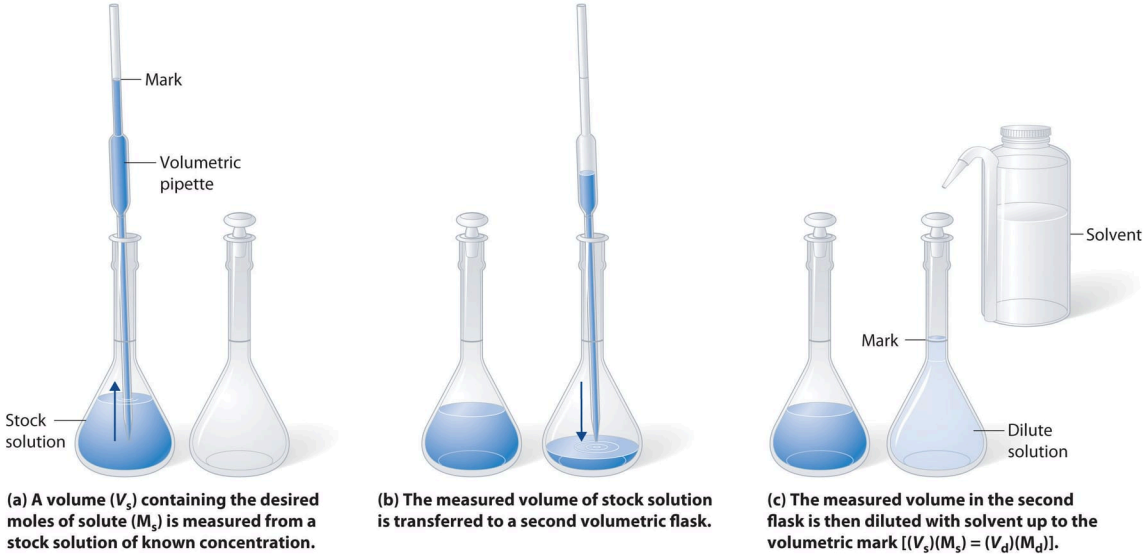
A solution of a desired concentration can also be prepared by diluting a small volume of a more concentrated solution with additional solvent. A stock solution is a commercially prepared solution of known concentration and is often used for this purpose. Diluting a stock solution is preferred because the alternative method, weighing out tiny amounts of solute, is difficult to carry out

with a high degree of accuracy. Dilution is also used to prepare solutions from substances that are sold as concentrated aqueous solutions, such as strong acids.

The procedure for preparing a solution of known concentration from a stock solution is shown in Figure 4.5.3. It requires calculating the number of moles of solute desired in the final volume of the more dilute solution and then calculating the volume of the stock solution that contains this amount of solute. Remember that diluting a given quantity of stock solution with solvent does *not* change the number of moles of solute present. The relationship between the volume and concentration of the stock solution and the volume and concentration of the desired diluted solution is therefore

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d) \tag{4.5.4}$$

where the subscripts s and *d* indicate the stock and dilute solutions, respectively. Example 4.5.4 demonstrates the calculations involved in diluting a concentrated stock solution.



(a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration.

(b) The measured volume of stock solution is transferred to a second volumetric flask.

(c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].

Figure 4.5.3: Preparation of a Solution of Known Concentration by Diluting a Stock Solution. (a) A volume (V_S) containing the desired moles of solute (M_S) is measured from a stock solution of known concentration. (b) The measured volume of stock solution is transferred to a second volumetric flask. (c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_S)(M_S) = (V_d)(M_d)$].

Example 4.5.4

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example 4.5.3?

Given: volume and molarity of dilute solution

Asked for: volume of stock solution

Strategy:

A. Calculate the number of moles of glucose contained in the indicated volume of dilute solution by multiplying the volume of the solution by its molarity.
B. To determine the volume of stock solution needed, divide the number of moles of glucose by the molarity of the stock solution.

Solution:

A The D5W solution in Example 4.5.3 was 0.310 M glucose. We begin by using Equation 4.5.4 to calculate the number of moles of glucose contained in 2500 mL of the solution:

$$moles\ glucose = 2500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.310\ mol\ glucose}{1\ \cancel{L}}\right) = 0.775\ mol\ glucose$$

B We must now determine the volume of the 3.00 M stock solution that contains this amount of glucose:

$$volume\ of\ stock\ soln = 0.775\ \cancel{mol\ glucose}\left(\frac{1\ L}{3.00\ \cancel{mol\ glucose}}\right) = 0.258\ L\ or\ 258\ mL$$

In determining the volume of stock solution that was needed, we had to divide the desired number of moles of glucose by the concentration of the stock solution to obtain the appropriate units. Also, the number of moles of solute in 258 mL of the stock solution is the same as the number of moles in 2500 mL of the more dilute solution; *only the amount of solvent has changed*. The answer we obtained makes sense: diluting the stock solution about tenfold increases its volume by about a factor of 10 (258 mL → 2500 mL). Consequently, the concentration of the solute must decrease by about a factor of 10, as it does (3.00 M → 0.310 M).

We could also have solved this problem in a single step by solving Equation 4.5.4 for V_s and substituting the appropriate values:

$$V_s = \frac{(V_d)(M_d)}{M_s} = \frac{(2.500\ L)(0.310\ \cancel{M})}{3.00\ \cancel{M}} = 0.258\ L$$

As we have noted, there is often more than one correct way to solve a problem.

Exercise 4.5.4

What volume of a 5.0 M NaCl stock solution is necessary to prepare 500 mL of normal saline solution (0.16 M NaCl)?

Answer available at the end of this section.

Ion Concentrations in Solution

In Example 4.5.2, the concentration of a solution containing 90.00 g of ammonium dichromate in a final volume of 250 mL were calculated to be 1.43 M. Let's consider in more detail exactly what that means. Ammonium dichromate is an ionic compound that contains two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion per formula unit. Like other ionic compounds, it is a strong electrolyte that dissociates in aqueous solution to give hydrated NH_4^+ and $Cr_2O_7^{2-}$ ions:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{H_2O(l)} 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \tag{4.5.5}$$

Thus 1 mol of ammonium dichromate formula units dissolves in water to produce 1 mol of $Cr_2O_7^{2-}$ anions and 2 mol of NH_4^+ cations (see Figure 4.5.4).

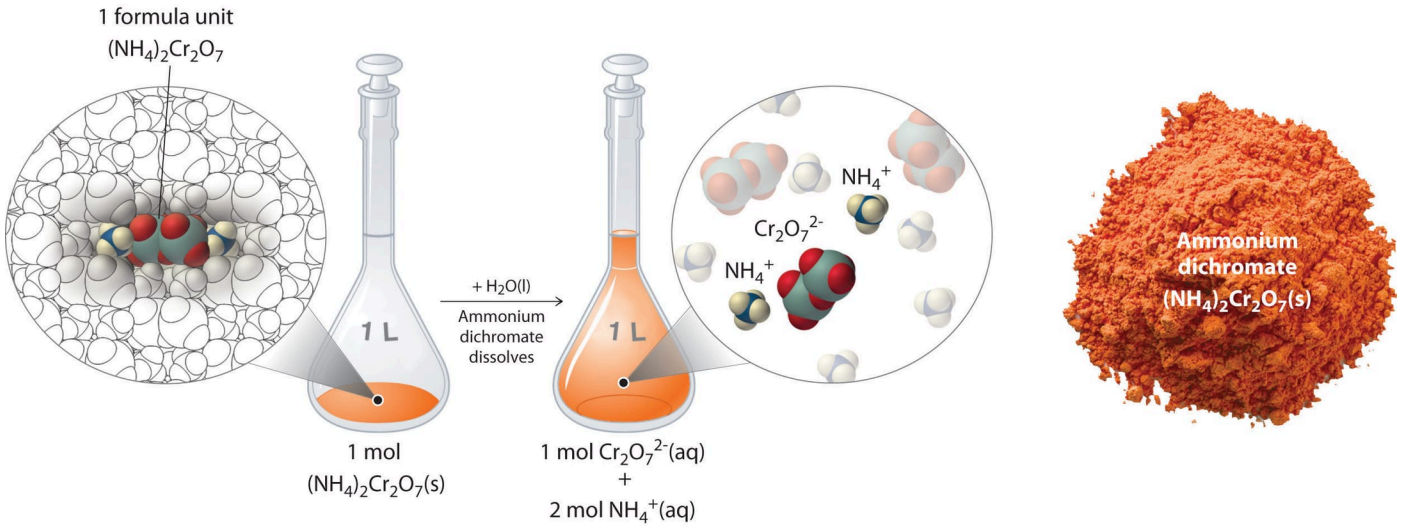


Figure 4.5.4: Dissolution of 1 mol of an Ionic Compound. In this case, dissolving 1 mol of $(NH_4)_2Cr_2O_7$ produces a solution that contains 1 mol of $Cr_2O_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)

1 mol of ammonium dichromate is shown in a 1 liter volumetric flask. The resulting volumetric flask on the right contains 1 liter of solution after being dissolved with water. Powdered form of ammonium dichromate is also included in diagram.

When carrying out a chemical reaction using a solution of a salt such as ammonium dichromate, it is important to know the concentration of each ion present in the solution. If a solution contains 1.43 M $(NH_4)_2Cr_2O_7$, then the concentration of $Cr_2O_7^{2-}$ must also be 1.43 M because there is one $Cr_2O_7^{2-}$ ion per formula unit. However, there are two NH_4^+ ions per formula unit, so the concentration of NH_4^+ ions is 2 × 1.43 M = 2.86 M. Because each formula unit of $(NH_4)_2Cr_2O_7$ produces *three* ions when dissolved in water ($2NH_4^+ + 1Cr_2O_7^{2-}$), the *total* concentration of ions in the solution is 3 × 1.43 M = 4.29 M.

YouTube Video

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Concentration of Ions in Solution from a Soluble Salt: Concentration of Ions in Solution from a Soluble Salt, YouTube(opens in new window) [youtu.be]

Example 4.5.5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

a. 0.21 M NaOH
b. 3.7 M $(CH_3)_2CHOH$
c. 0.032 M $In(NO_3)_3$

Given: molarity

Asked for: concentrations

Strategy:

A Classify each compound as either a strong electrolyte or a nonelectrolyte.

B If the compound is a nonelectrolyte, its concentration is the same as the molarity of the solution. If the compound is a strong electrolyte, determine the number of each ion contained in one formula unit. Find the concentration of each species by multiplying the number of each ion by the molarity of the solution.

Solution:

1. Sodium hydroxide is an ionic compound that is a strong electrolyte (and a strong base) in aqueous solution: $NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$

   B Because each formula unit of NaOH produces one Na^+ ion and one OH^- ion, the concentration of each ion is the same as the concentration of NaOH: [Na^+] = 0.21 M and [OH^-] = 0.21 M.

2. **A** The formula $(CH_3)_2CHOH$ represents 2-propanol (isopropyl alcohol) and contains the –OH group, so it is an alcohol. Recall from Section 4.1 that alcohols are covalent compounds that dissolve in water to give solutions of neutral molecules. Thus alcohols are nonelectrolytes.

   B The only solute species in solution is therefore $(CH_3)_2CHOH$ molecules, so [$(CH_3)_2CHOH$] = 3.7 M.

3. **A** Indium nitrate is an ionic compound that contains In^{3+} ions and NO_3^- ions, so we expect it to behave like a strong electrolyte in aqueous solution:

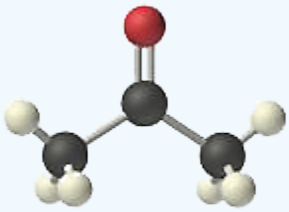
   $$In(NO_3)_3(s) \xrightarrow{H_2O(l)} In^{3+}(aq) + 3NO_3^-(aq)$$

   B One formula unit of $In(NO_3)_3$ produces one In^{3+} ion and three NO_3^- ions, so a 0.032 M $In(NO_3)_3$ solution contains 0.032 M In^{3+} and 3 × 0.032 M = 0.096 M NO_3^-—that is, [In^{3+}] = 0.032 M and [NO_3^-] = 0.096 M.

Exercise 4.5.5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

a. 0.0012 M $Ba(OH)_2$
b. 0.17 M Na_2SO_4
c. 0.50 M $(CH_3)_2CO$, commonly known as acetone



Acetone
$(CH_3)_2CO$

Answer a available at the end of this section.

Summary

Solution concentrations are typically expressed as molarities and can be prepared by dissolving a known mass of solute in a solvent or diluting a stock solution.

- **definition of molarity:**

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution}$$

- **relationship among volume, molarity, and moles**:

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles$$

- **relationship between volume and concentration of stock and dilute solutions**:

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d)$$

The **concentration** of a substance is the quantity of solute present in a given quantity of solution. Concentrations are usually expressed in terms of **molarity**, defined as the number of moles of solute in 1 L of solution. Solutions of known concentration can be prepared either by dissolving a known mass of solute in a solvent and diluting to a desired final volume or by diluting the appropriate volume of a more concentrated solution (a **stock solution**) to the desired final volume.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise $4.5.1$**: Calculating Moles from Concentration of Alanine**

41.6 mmol

Exercise $4.5.2$

$$(NH_4)_2Cr_2O_7 = 1.43\ M$$

Exercise $4.5.3$

2.3 g NaCl

Exercise $4.5.4$

16 mL

Exercise $4.5.5$

$[Ba^{2+}] = 0.0012\ M;\ [OH^-] = 0.0024\ M$

$[Na^+] = 0.34\ M;\ [SO_4^{2-}] = 0.17\ M$

$[(CH_3)_2CO] = 0.50\ M$

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4.6: Solution Stoichiometry and Chemical Analysis

Learning Objectives

- To use titration methods to analyze solutions quantitatively.

To determine the amounts or concentrations of substances present in a sample, chemists use a combination of chemical reactions and stoichiometric calculations in a methodology called quantitative analysis. Suppose, for example, we know the identity of a certain compound in a solution but not its concentration. If the compound reacts rapidly and completely with another reactant, we may be able to use the reaction to determine the concentration of the compound of interest. In a **titration**, a carefully measured volume of a solution of known concentration, called the titrant, is added to a measured volume of a solution containing a compound whose concentration is to be determined (the unknown). The reaction used in a titration can be an acid–base reaction, a precipitation reaction, or an oxidation–reduction reaction. In all cases, the reaction chosen for the analysis must be fast, complete, and specific; that is, only the compound of interest should react with the titrant. The **equivalence point** is reached when a stoichiometric amount of the titrant has been added—the amount required to react completely with the unknown.

Determining the Concentration of an Unknown Solution Using a Titration

The chemical nature of the species present in the unknown dictates which type of reaction is most appropriate and also how to determine the equivalence point. The volume of titrant added, its concentration, and the coefficients from the balanced chemical equation for the reaction allow us to calculate the total number of moles of the unknown in the original solution. Because we have measured the volume of the solution that contains the unknown, we can calculate the molarity of the unknown substance. This procedure is summarized graphically here:

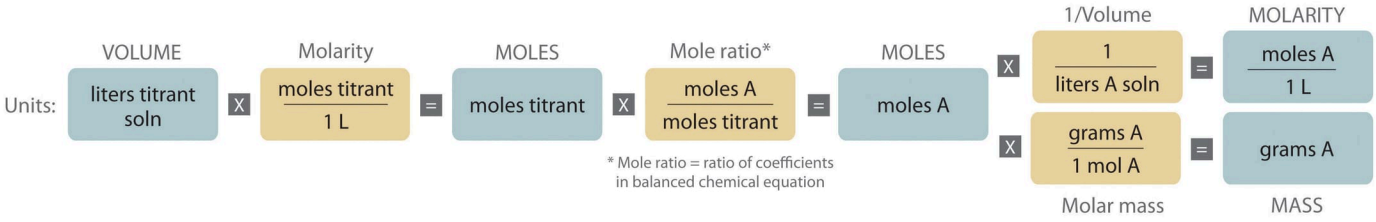


Figure $4.6.1$***:*** *Dimensional Analysis flowchart for titration problems.*

Example $4.6.1$: Potassium Permanganate

The calcium salt of oxalic acid [$Ca(O_2CCO_2)$] is found in the sap and leaves of some vegetables, including spinach and rhubarb, and in many ornamental plants. Because oxalic acid and its salts are toxic, when a food such as rhubarb is processed commercially, the leaves must be removed, and the oxalate content carefully monitored.

The reaction of MnO_4^- with oxalic acid (HO_2CCO_2H) in acidic aqueous solution produces Mn^{2+} and CO_2:

$$\underset{purple}{MnO_4^-\,(aq) + HO_2CCO_2H\,(aq)} \rightarrow \underset{colorless}{Mn^{2+}\,(aq)} + CO_2\,(g) + H_2O\,(l)$$

Because this reaction is rapid and goes to completion, potassium permanganate ($KMnO_4$) is widely used as a reactant for determining the concentration of oxalic acid.

Suppose you stirred a 10.0 g sample of canned rhubarb with enough dilute H_2SO_4(aq) to obtain 127 mL of colorless solution. Because the added permanganate is rapidly consumed, adding small volumes of a 0.0247 M $KMnO_4$ solution, which has a deep purple color, to the rhubarb extract does not initially change the color of the extract. When 15.4 mL of the permanganate solution have been added, however, the solution becomes a faint purple due to the presence of a slight

excess of permanganate. If we assume that oxalic acid is the only species in solution that reacts with permanganate, what percentage of the mass of the original sample was calcium oxalate? The video below demonstrates the titration when small, measured amounts of a known permaganate solution are added. At the endpoint, the number of moles of permaganate added equals the number of moles of oxalate in the solution, thus determining how many moles of oxalate we started with.

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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Given: equation, mass of sample, volume of solution, and molarity and volume of titrant

Asked for: mass percentage of unknown in sample

Strategy:

A. Balance the chemical equation for the reaction using oxidation states.
B. Calculate the number of moles of permanganate consumed by multiplying the volume of the titrant by its molarity. Then calculate the number of moles of oxalate in the solution by multiplying by the ratio of the coefficients in the balanced chemical equation. Because calcium oxalate contains a 1:1 ratio of Ca^{2+}:$^{-}O_2CCO_2^{-}$, the number of moles of oxalate in the solution is the same as the number of moles of calcium oxalate in the original sample.
C. Find the mass of calcium oxalate by multiplying the number of moles of calcium oxalate in the sample by its molar mass. Divide the mass of calcium oxalate by the mass of the sample and convert to a percentage to calculate the percentage by mass of calcium oxalate in the original sample.

Solution:

A As in all other problems of this type, the first requirement is a balanced chemical equation for the reaction. Using oxidation states gives

$$2MnO_4^-(aq) + 5HO_2CCO_2H(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Thus each mole of MnO_4^- added consumes 2.5 mol of oxalic acid.

B Because we know the concentration of permanganate (0.0247 M) and the volume of permanganate solution that was needed to consume all the oxalic acid (15.4 mL), we can calculate the number of moles of MnO_4^- consumed. To do this we first convert the volume in mL to a volume in liters. Then simply multiplying the molarity of the solution by the volume in liters we find the number of moles of MnO_4^-

$$15.4 \cancel{mL}\left(\frac{1 \cancel{L}}{1000 \cancel{mL}}\right)\left(\frac{0.0247\ mol\ MnO_4^-}{1 \cancel{L}}\right) = 3.80 \times 10^4\ mol\ MnO_4^-$$

The number of moles of oxalic acid, and thus oxalate, present can be calculated from the mole ratio of the reactants in the balanced chemical equation. We can abbreviate the table needed to calculate the number of moles of oxalic acid in the

$$moles\ HO_2CCO_2H = 3.80 \times 10^{-4}\ \cancel{mol\ MnO_4^-}\left(\frac{5\ mol\ HO_2CCO_2H}{2\ \cancel{mol\ MnO_4^-}}\right) \tag{4.6.1}$$

$$= 9.50 \times 10^{-4}\ mol\ HO_2CCO_2H \tag{4.6.2}$$

C The problem asks for the *percentage* of calcium oxalate by mass in the original 10.0 g sample of rhubarb, so we need to know the mass of calcium oxalate that produced 9.50×10^{-4} mol of oxalic acid. Because calcium oxalate is $Ca(O_2CCO_2)$, 1 mol of calcium oxalate gave 1 mol of oxalic acid in the initial acid extraction:

$$Ca(O_2CCO_2)(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + HO_2CCO_2H(aq)$$

The mass of calcium oxalate originally present was thus

$$mass\ of\ CaC_2O_4 = 9.50 \times 10^{-4}\ \cancel{mol\ HO_2CCO_2H} \left(\frac{1\ \cancel{mol\ CaC_2O_4}}{1\ \cancel{mol\ HO_2CCO_2H}}\right)\left(\frac{128.10\ g\ CaC_2O_4}{1\ \cancel{mol\ CaC_2O_4}}\right) \tag{4.6.3}$$

$$= 0.122\ g\ CaC_2O_4 \tag{4.6.4}$$

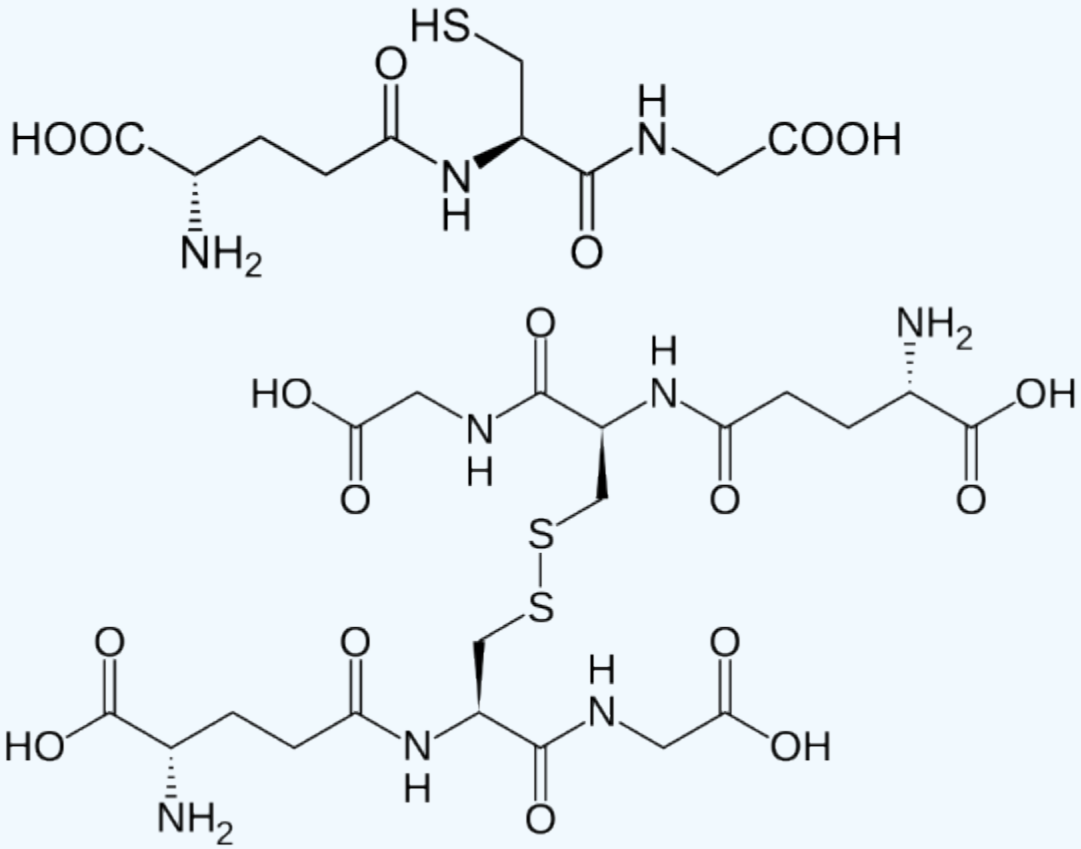
The original sample contained 0.122 g of calcium oxalate per 10.0 g of rhubarb. The percentage of calcium oxalate by mass was thus

$$\%CaC_2O_4 = \frac{0.122\ g}{10.0\ g} \times 100 = 1.22\%$$

Because the problem asked for the percentage by mass of calcium oxalate in the original sample rather than for the *concentration* of oxalic acid in the extract, we do not need to know the volume of the oxalic acid solution for this calculation.

Exercise 4.6.1: Glutathione

Glutathione is a low-molecular-weight compound found in living cells that is produced naturally by the liver. Health-care providers give glutathione intravenously to prevent side effects of chemotherapy and to prevent kidney problems after heart bypass surgery. Its structure is as follows:



Glutathione is found in two forms: one abbreviated as (left) GSH (indicating the presence of an –SH group) and the other (right) as GSSG (the *disulfide* form, in which an S–S bond links two glutathione units). The GSH form is easily oxidized to GSSG with elemental iodine:

$$2\,\mathrm{GSH\,(aq)} + \mathrm{I_2\,(aq)} \rightarrow \mathrm{GSSG\,(aq)} + 2\,\mathrm{HI\,(aq)}$$

A small amount of soluble starch is added as an indicator. Because starch reacts with excess I_2 to give an intense blue color, the appearance of a blue color indicates that the equivalence point of the reaction has been reached.

Adding small volumes of a 0.0031 M aqueous solution of I_2 to 194 mL of a solution that contains glutathione and a trace of soluble starch initially causes no change. After 16.3 mL of iodine solution have been added, however, a permanent pale blue color appears because of the formation of the starch-iodine complex. What is the concentration of glutathione in the original solution?

Answer available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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Limiting Reactant Problems Using Molarities: Limiting Reactant Problems Using Molarities, YouTube(opens in new window) [youtu.be]

Standard Solutions

In Example 4.6.1, the concentration of the titrant (I_2) was accurately known. The accuracy of any titration analysis depends on an accurate knowledge of the concentration of the titrant. Most titrants are first *standardized*; that is, their concentration is measured by titration with a standard solution, which is a solution whose concentration is known precisely. Only pure crystalline compounds that do not react with water or carbon dioxide are suitable for use in preparing a standard solution. One such compound is potassium hydrogen phthalate (KHP), a weak monoprotic acid suitable for standardizing solutions of bases such as sodium hydroxide. The reaction of KHP with NaOH is a simple acid–base reaction. If the concentration of the KHP solution is known accurately and the titration of a NaOH solution with the KHP solution is carried out carefully, then the concentration of the NaOH solution can be calculated precisely. The standardized NaOH solution can then be used to titrate a solution of an acid whose concentration is unknown.

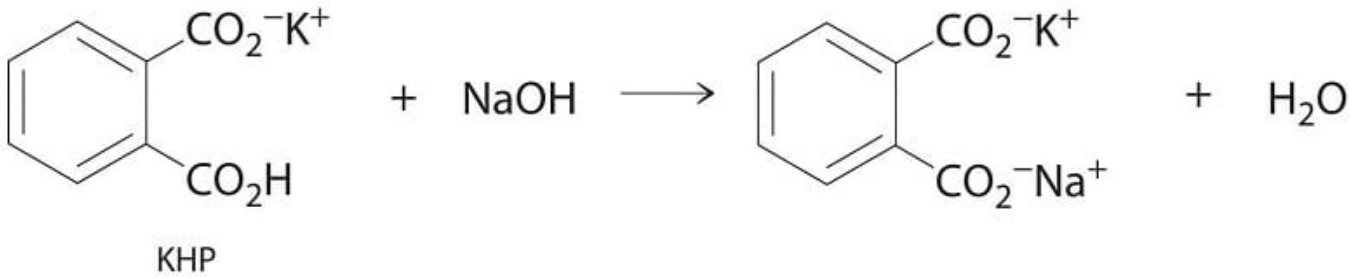


Figure 4.6.2: The reaction of KHP with NaOH. As with all acid-base reactions, a salt is formed.

Answers

Exercise 4.6.1: Glutathione

5.2×10^{-4} M

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4.E: Reactions in Aqueous Solution (Exercises)

4.1: General Properties of Aqueous Solutions

Conceptual Problems

1. What are the advantages to carrying out a reaction in solution rather than simply mixing the pure reactants?
2. What types of compounds dissolve in polar solvents?
3. Describe the charge distribution in liquid water. How does this distribution affect its physical properties?
4. Must a molecule have an asymmetric charge distribution to be polar? Explain your answer.
5. Why are many ionic substances soluble in water?
6. Explain the phrase *like dissolves like*.
7. What kinds of covalent compounds are soluble in water?
8. Why do most aromatic hydrocarbons have only limited solubility in water? Would you expect their solubility to be higher, lower, or the same in ethanol compared with water? Why?
9. Predict whether each compound will dissolve in water and explain why.
    a. toluene
    b. acetic acid
    c. sodium acetate
    d. butanol
    e. pentanoic acid
10. Predict whether each compound will dissolve in water and explain why.
    a. ammonium chloride
    b. 2-propanol
    c. heptane
    d. potassium dichromate
    e. 2-octanol
11. Given water and toluene, predict which is the better solvent for each compound and explain your reasoning.
    a. sodium cyanide
    b. benzene
    c. acetic acid
    d. sodium ethoxide (CH_3CH_2ONa)
12. Of water and toluene, predict which is the better solvent for each compound and explain your reasoning.
    a. *t*-butanol
    b. calcium chloride
    c. sucrose
    d. cyclohexene
13. Compound *A* is divided into three equal samples. The first sample does not dissolve in water, the second sample dissolves only slightly in ethanol, and the third sample dissolves completely in toluene. What does this suggest about the polarity of *A*?

14. You are given a mixture of three solid compounds—*A*, *B*, and *C*—and are told that *A* is a polar compound, *B* is slightly polar, and *C* is nonpolar. Suggest a method for separating these three compounds.

15. A laboratory technician is given a sample that contains only sodium chloride, sucrose, and cyclodecanone (a ketone). You must tell the technician how to separate these three compounds from the mixture. What would you suggest?

16. Many over-the-counter drugs are sold as ethanol/water solutions rather than as purely aqueous solutions. Give a plausible reason for this practice.

17. What distinguishes a weak electrolyte from a strong electrolyte?

18. Which organic groups result in aqueous solutions that conduct electricity?

19. It is considered highly dangerous to splash barefoot in puddles during a lightning storm. Why?

20. Which solution(s) would you expect to conduct electricity well? Explain your reasoning.

    a. an aqueous solution of sodium chloride
    b. a solution of ethanol in water
    c. a solution of calcium chloride in water
    d. a solution of sucrose in water

21. Which solution(s) would you expect to conduct electricity well? Explain your reasoning.

    a. an aqueous solution of acetic acid
    b. an aqueous solution of potassium hydroxide
    c. a solution of ethylene glycol in water
    d. a solution of ammonium chloride in water

22. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in an aqueous solution? Explain your reasoning.

    a. potassium hydroxide
    b. ammonia
    c. calcium chloride
    d. butanoic acid

23. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in an aqueous solution? Explain your reasoning.

    a. magnesium hydroxide
    b. butanol
    c. ammonium bromide
    d. pentanoic acid

24. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in aqueous solution? Explain your reasoning.

    a. H_2SO_4
    b. diethylamine
    c. 2-propanol
    d. ammonium chloride
    e. propanoic acid

Conceptual Answers

1.
2.
3.

4.

5. Ionic compounds such as NaCl are held together by electrostatic interactions between oppositely charged ions in the highly ordered solid. When an ionic compound dissolves in water, the partially negatively charged oxygen atoms of the H_2O molecules surround the cations, and the partially positively charged hydrogen atoms in H_2O surround the anions. The favorable electrostatic interactions between water and the ions compensate for the loss of the electrostatic interactions between ions in the solid.

6.
7.
8.
9. a. Because toluene is an aromatic hydrocarbon that lacks polar groups, it is unlikely to form a homogenous solution in water.
   b. Acetic acid contains a carboxylic acid group attached to a small alkyl group (a methyl group). Consequently, the polar characteristics of the carboxylic acid group will be dominant, and acetic acid will form a homogenous solution with water.
   c. Because most sodium salts are soluble, sodium acetate should form a homogenous solution with water.
   d. Like all alcohols, butanol contains an –OH group that can interact well with water. The alkyl group is rather large, consisting of a 4-carbon chain. In this case, the nonpolar character of the alkyl group is likely to be as important as the polar character of the –OH, decreasing the likelihood that butanol will form a homogeneous solution with water.
   e. Like acetic acid, pentanoic acid is a carboxylic acid. Unlike acetic acid, however, the alkyl group is rather large, consisting of a 4-carbon chain as in butanol. As with butanol, the nonpolar character of the alkyl group is likely to be as important as the polar character of the carboxylic acid group, making it unlikely that pentanoic acid will form a homogeneous solution with water. (In fact, the solubility of both butanol and pentanoic acid in water is quite low, only about 3 g per 100 g water at 25°C.)
10.
11.
12.
13.
14.
15.
16.

17. An *electrolyte* is any compound that can form ions when it dissolves in water. When a strong electrolyte dissolves in water, it dissociates completely to give the constituent ions. In contrast, when a weak electrolyte dissolves in water, it produces relatively few ions in solution.

4.2: Precipitation Reactions

Conceptual Problems

0. What information can be obtained from a complete ionic equation that cannot be obtained from the overall chemical equation?

1. Predict whether mixing each pair of solutions will result in the formation of a precipitate. If so, identify the precipitate.

   a. $FeCl_2(aq) + Na_2S(aq)$
   b. $NaOH(aq) + H_3PO_4(aq)$
   c. $ZnCl_2(aq) + (NH_4)_2S(aq)$

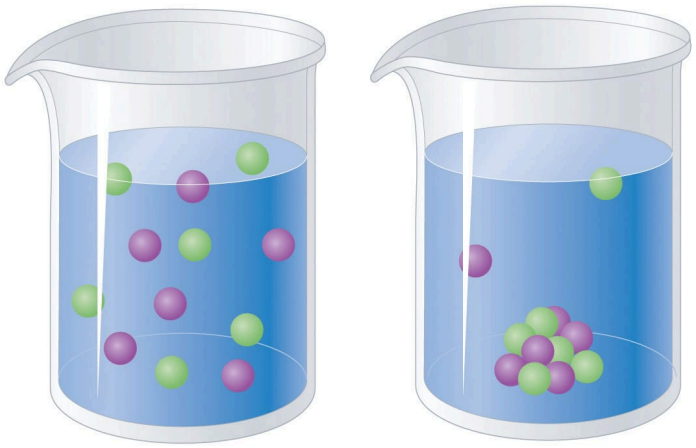
2. Predict whether mixing each pair of solutions will result in the formation of a precipitate. If so, identify the precipitate.

   a. $KOH(aq) + H_3PO_4(aq)$
   b. $K_2CO_3(aq) + BaCl_2(aq)$
   c. $Ba(NO_3)_2(aq) + Na_2SO_4(aq)$

3. Which representation best corresponds to an aqueous solution originally containing each of the following?

a. 1 M NH_4Cl
b. 1 M NaO_2CCH_3
c. 1 M NaOH + 1 M HCl

d. 1 M $Ba(OH)_2$ + 1 M H_2SO_4



(1) (2)

4. Which representation in Problem 3 best corresponds to an aqueous solution originally containing each of the following?

a. 1 M CH_3CO_2H + 1 M NaOH
b. 1 M NH_3 + 1 M HCl
c. 1 M Na_2CO_3 + 1 M H_2SO_4
d. 1 M $CaCl_2$ + 1 M H_3PO_4

Conceptual Answer

3

a. 1
b. 1
c. 1
d. 2

Numerical Problems

1. What mass of precipitate would you expect to obtain by mixing 250 mL of a solution containing 4.88 g of Na_2CrO_4 with 200 mL of a solution containing 3.84 g of $AgNO_3$? What is the final nitrate ion concentration?

2. Adding 10.0 mL of a dilute solution of zinc nitrate to 246 mL of 2.00 M sodium sulfide produced 0.279 g of a precipitate. How many grams of zinc(II) nitrate and sodium sulfide were consumed to produce this quantity of product? What was the concentration of each ion in the original solutions? What is the concentration of the sulfide ion in solution after the precipitation reaction, assuming no further reaction?

Numerical Answer

1. 3.75 g Ag_2CrO_4; 5.02×10^{-2} M nitrate

4.3: Acid-Base Reactions

Conceptual Problems

1. Why was it necessary to expand on the Arrhenius definition of an acid and a base? What specific point does the Brønsted–Lowry definition address?

2. State whether each compound is an acid, a base, or a salt.

   a. $CaCO_3$
   b. $NaHCO_3$
   c. H_2SO_4
   d. $CaCl_2$
   e. $Ba(OH)_2$

3. State whether each compound is an acid, a base, or a salt.

   a. NH_3
   b. NH_4Cl
   c. H_2CO_3
   d. CH_3COOH
   e. NaOH

4. Classify each compound as a strong acid, a weak acid, a strong base, or a weak base in aqueous solution.

   a. sodium hydroxide
   b. acetic acid
   c. magnesium hydroxide
   d. tartaric acid
   e. sulfuric acid
   f. ammonia
   g. hydroxylamine (NH_2OH)
   h. hydrocyanic acid

5. Decide whether each compound forms an aqueous solution that is strongly acidic, weakly acidic, strongly basic, or weakly basic.

   a. propanoic acid
   b. hydrobromic acid
   c. methylamine
   d. lithium hydroxide
   e. citric acid
   f. sodium acetate
   g. ammonium chloride
   h. barium hydroxide

6. What is the relationship between the strength of an acid and the strength of the conjugate base derived from that acid? Would you expect the $CH_3CO_2^-$ ion to be a strong base or a weak base? Why? Is the hydronium ion a strong acid or a weak acid? Explain your answer.

7. What are the products of an acid–base reaction? Under what circumstances is one of the products a gas?

8. Explain how an aqueous solution that is strongly basic can have a pH, which is a measure of the *acidity* of a solution.

Answer

1.
2.
3.
4.
5. a. weakly acidic
   b. strongly acidic
   c. weakly basic
   d. strongly basic
   e. weakly acidic
   f. weakly basic
   g. weakly acidic
   h. strongly basic
6.
7.
8.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 3 (section 4.1 "Aqueous Solutions") before proceeding to the Numerical Problems.

1. Derive an equation to relate the hydrogen ion concentration to the molarity of a solution of a strong monoprotic acid.

2. Derive an equation to relate the hydroxide ion concentration to the molarity of a solution of

   a. a group I hydroxide.
   b. a group II hydroxide.

3. Given the following salts, identify the acid and the base in the neutralization reactions and then write the complete ionic equation:

   a. barium sulfate
   b. lithium nitrate
   c. sodium bromide
   d. calcium perchlorate

4. What is the pH of each solution?

   a. 5.8×10^{-3} mol of HNO_3 in 257 mL of water
   b. 0.0079 mol of HI in 750 mL of water
   c. 0.011 mol of $HClO_4$ in 500 mL of water
   d. 0.257 mol of HBr in 5.00 L of water

5. What is the hydrogen ion concentration of each substance in the indicated pH range?

   a. black coffee (pH 5.10)
   b. milk (pH 6.30–7.60)
   c. tomatoes (pH 4.00–4.40)

6. What is the hydrogen ion concentration of each substance in the indicated pH range?

   a. orange juice (pH 3–4)
   b. fresh egg white (pH 7.60–7.80)
   c. lemon juice (pH 2.20–2.40)

7. What is the pH of a solution prepared by diluting 25.00 mL of 0.879 M HCl to a volume of 555 mL?

8. Vinegar is primarily an aqueous solution of acetic acid. Commercial vinegar typically contains 5.0 g of acetic acid in 95.0 g of water. What is the concentration of commercial vinegar? If only 3.1% of the acetic acid dissociates to $CH_3CO_2^-$ and H^+, what is the pH of the solution? (Assume the density of the solution is 1.00 g/mL.)

9. If a typical household cleanser is 0.50 M in strong base, what volume of 0.998 M strong monoprotic acid is needed to neutralize 50.0 mL of the cleanser?

10. A 25.00 mL sample of a 0.9005 M solution of HCl is diluted to 500.0 mL. What is the molarity of the final solution? How many milliliters of 0.223 M NaOH are needed to neutralize 25.00 mL of this final solution?

11. If 20.0 mL of 0.10 M NaOH are needed to neutralize 15.0 mL of gastric fluid, what is the molarity of HCl in the fluid? (Assume all the acidity is due to the presence of HCl.) What other base might be used instead of NaOH?

12. Malonic acid ($C_3H_4O_4$) is a diprotic acid used in the manufacture of barbiturates. How many grams of malonic acid are in a 25.00 mL sample that requires 32.68 mL of 1.124 M KOH for complete neutralization to occur? Malonic acid is a dicarboxylic acid; propose a structure for malonic acid.

13. Describe how you would prepare 500 mL of a 1.00 M stock solution of HCl from an HCl solution that is 12.11 M. Using your stock solution, how would you prepare 500 mL of a solution that is 0.012 M in HCl?

14. Given a stock solution that is 8.52 M in HBr, describe how you would prepare a 500 mL solution with each concentration.

    a. 2.50 M
    b. 4.00×10^{-3} M
    c. 0.989 M

15. How many moles of solute are contained in each?

    a. 25.00 mL of 1.86 M NaOH
    b. 50.00 mL of 0.0898 M HCl
    c. 13.89 mL of 0.102 M HBr

16. A chemist needed a solution that was approximately 0.5 M in HCl but could measure only 10.00 mL samples into a 50.00 mL volumetric flask. Propose a method for preparing the solution. (Assume that concentrated HCl is 12.0 M.)

17. Write the balanced chemical equation for each reaction.

    a. perchloric acid with potassium hydroxide
    b. nitric acid with calcium hydroxide

18. Write the balanced chemical equation for each reaction.

    a. solid strontium hydroxide with hydrobromic acid
    b. aqueous sulfuric acid with solid sodium hydroxide

19. A neutralization reaction gives calcium nitrate as one of the two products. Identify the acid and the base in this reaction. What is the second product? If the product had been cesium iodide, what would have been the acid and the base? What is the complete ionic equation for each reaction?

Answers

1. $[H_3O^+] = [HA]$ M

2.

3. a. H_2SO_4 and $Ba(OH)_2$; $2H^+ + SO_4^{2-} + Ba^{2+} + 2OH^- \rightarrow 2H_2O + Ba^{2+} + SO_4^{2-}$
   b. HNO_3 and LiOH; $H^+ + NO_3^- + Li^+ + OH^- \rightarrow H_2O + Li^+ + NO_3^-$
   c. HBr and NaOH; $H^+ + Br^- + Na^+ + OH^- \rightarrow H_2O + Na^+ + Br^-$

d. $HClO_4$ and $Ca(OH)_2$; $2H^+ + 2ClO_4^- + Ca^{2+} + 2OH^- \rightarrow 2H_2O + Ca^{2+} + 2ClO_4^-$

4.

5. a. 7.9×10^{-6} M H^+
   b. 5.0×10^{-7} to 2.5×10^{-8} M H^+
   c. 1.0×10^{-4} to 4.0×10^{-5} M H^+

6.

7. pH = 1.402

8.

9. 25 mL

10.

11. 0.13 M HCl; magnesium carbonate, $MgCO_3$, or aluminum hydroxide, $Al(OH)_3$

12.

13. 1.00 M solution: dilute 41.20 mL of the concentrated solution to a final volume of 500 mL. 0.012 M solution: dilute 12.0 mL of the 1.00 M stock solution to a final volume of 500 mL.

14.

15. a. 4.65×10^{-2} mol NaOH
    b. 4.49×10^{-3} mol HCl
    c. 1.42×10^{-3} mol HBr

16.

17. a. $HClO_4 + KOH \rightarrow KClO_4 + H_2O$
    b. $2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$

18.

19. The acid is nitric acid, and the base is calcium hydroxide. The other product is water.

$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$$

The acid is hydroiodic acid, and the base is cesium hydroxide. The other product is water.

$$HI + CsOH \rightarrow CsI + H_2O$$

The complete ionic equations are

$$2H^+ + 2NO_3^- + Ca^{2+} + 2OH^- \rightarrow Ca^{2+} + 2NO_3^- + H_2O$$
$$H^+ + I^- + Cs^+ + OH^- \rightarrow Cs^+ + I^- + H_2O$$

4.4: Oxidation-Reduction Reactions

Conceptual Problems

1. Which elements in the periodic table tend to be good oxidants? Which tend to be good reductants?

2. If two compounds are mixed, one containing an element that is a poor oxidant and one with an element that is a poor reductant, do you expect a redox reaction to occur? Explain your answer. What do you predict if one is a strong oxidant and the other is a weak reductant? Why?

3. In each redox reaction, determine which species is oxidized and which is reduced:

a. $Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$
b. $Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$
c. $BrO_3^-(aq) + 2MnO_2(s) + H_2O(l) \rightarrow Br^-(aq) + 2MnO_4^-(aq) + 2H^+(aq)$

4. Single-displacement reactions are a subset of redox reactions. In this subset, what is oxidized and what is reduced? Give an example of a redox reaction that is *not* a single-displacement reaction.

Conceptual Solutions

1. In the periodic table, the trend for oxidation increases towards the top-right of the table, while the trend for reduction increases towards the bottom-left. That is to say, the nonmetals and metalloids (with the exception of Noble Gases) tend to be better oxidants, and alkali and transition metals tend to be better reductants.

2. If the compounds mixed are both poor oxidants and poor reductants, no redox reaction will occur. The poor oxidizing agent has a weak ability to gain electrons, while the reducing agent has a weak ability to donate electrons. Due to this, no electrons (or very few electrons) will be transferred, and no reaction will occur. If one compound is a strong oxidant and the other is a weak reductant, the reaction will progress, but not as far as it would have with a strong reductant. Some reductants, such as gold, are so weak that only the strongest of oxidants can oxidize them.

3. Which is Oxidized and Reduced:

    1. Zn is oxidized, and H is reduced.
    2. Cu is oxidized, and N is reduced.
    3. Mn is oxidized, and Br is reduced.

4. A single-displacement reaction occurs when one "free" element replaces another similar element in a compound. What is oxidized and what is reduced depends on the elements in question. For example, in the single-displacement reaction $Zn(s)+2HCl(aq) \rightarrow ZnCl_2(aq)+H_2(g)$, the free element Zinc is oxidized while Hydrogen is reduced. In $Cl_2(g)+2NaBr(aq) \rightarrow 2NaCl(aq)+Br_2(l)$, on the other hand, the free element Chlorine is reduced while Bromine is oxidized.

    1. An example of a non-single-displacement reaction is a *double*-displacement reaction, such as: $2KI(aq)+Pb(NO_3)_2(aq) \rightarrow 2KNO_3(aq)+PbI_2(s)$

Numerical Problems

1. Balance each redox reaction under the conditions indicated.

    a. $CuS(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + NO(g)$; acidic solution
    b. $Ag(s) + HS^-(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2S(s) + Cr(OH)_3(s)$; basic solution
    c. $Zn(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + H_2(g)$; acidic solution
    d. $O_2(g) + Sb(s) \rightarrow H_2O_2(aq) + SbO_2^-(aq)$; basic solution
    e. $UO_2^{2+}(aq) + Te(s) \rightarrow U^{4+}(aq) + TeO_4^{2-}(aq)$; acidic solution

2. Balance each redox reaction under the conditions indicated.

    a. $MnO_4^-(aq) + S_2O_3^{2-}(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq)$; acidic solution
    b. $Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$; acidic solution
    c. $Fe(s) + CrO_4^{2-}(aq) \rightarrow Fe_2O_3(s) + Cr_2O_3(s)$; basic solution
    d. $Cl_2(aq) \rightarrow ClO_3^-(aq) + Cl^-(aq)$; acidic solution
    e. $CO_3^{2-}(aq) + N_2H_4(aq) \rightarrow CO(g) + N_2(g)$; basic solution

3. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation; then write the complete ionic equation for the reaction.

a. Platinum wire is dipped in hydrochloric acid.
b. Manganese metal is added to a solution of iron(II) chloride.
c. Tin is heated with steam.
d. Hydrogen gas is bubbled through a solution of lead(II) nitrate.

4. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation; then write the complete ionic equation for the reaction.

   a. A few drops of $NiBr_2$ are dropped onto a piece of iron.
   b. A strip of zinc is placed into a solution of HCl.
   c. Copper is dipped into a solution of $ZnCl_2$.
   d. A solution of silver nitrate is dropped onto an aluminum plate.

5. Dentists occasionally use metallic mixtures called *amalgams* for fillings. If an amalgam contains zinc, however, water can contaminate the amalgam as it is being manipulated, producing hydrogen gas under basic conditions. As the filling hardens, the gas can be released, causing pain and cracking the tooth. Write a balanced chemical equation for this reaction.

6. Copper metal readily dissolves in dilute aqueous nitric acid to form blue $Cu^{2+}(aq)$ and nitric oxide gas.

   a. What has been oxidized? What has been reduced?
   b. Balance the chemical equation.

7. Classify each reaction as an acid–base reaction, a precipitation reaction, or a redox reaction, or state if there is no reaction; then complete and balance the chemical equation:

   a. $Pt^{2+}(aq) + Ag(s) \rightarrow$
   b. $HCN(aq) + NaOH(aq) \rightarrow$
   c. $Fe(NO_3)_3(aq) + NaOH(aq) \rightarrow$
   d. $CH_4(g) + O_2(g) \rightarrow$

8. Classify each reaction as an acid–base reaction, a precipitation reaction, or a redox reaction, or state if there is no reaction; then complete and balance the chemical equation:

   a. $Zn(s) + HCl(aq) \rightarrow$
   b. $HNO_3(aq) + AlCl_3(aq) \rightarrow$
   c. $K_2CrO_4(aq) + Ba(NO_3)_2(aq) \rightarrow$
   d. $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$Conceptual

Numerical Solutions

1. Balanced Redox Reactions:
   1. $3CuS(s) + 8NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 3SO_4^{2-}(aq) + 8NO(g) + 4H_2O(l)$
   2. $6Ag(s) + 2CrO_4^{2-}(aq) + 3HS^-(aq) + 5H_2O(l) \rightarrow 3Ag_2S(s) + 2Cr(OH)_3(s) + 7OH^-(aq)$
   3. $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
   4. $2Sb(s) + 3O_2(g) + 2H_2O(l) + 2OH^-(aq) \rightarrow 2SbO_2^-(aq) + 3H_2O_2(aq)$
   5. $Te(s) + 3UO_2^{2+}(aq) + 4H^+(aq) \rightarrow TeO_4^{2-}(aq) + 3U^{4+}(aq) + 2H_2O(l)$

4.5: Concentration of Solutions

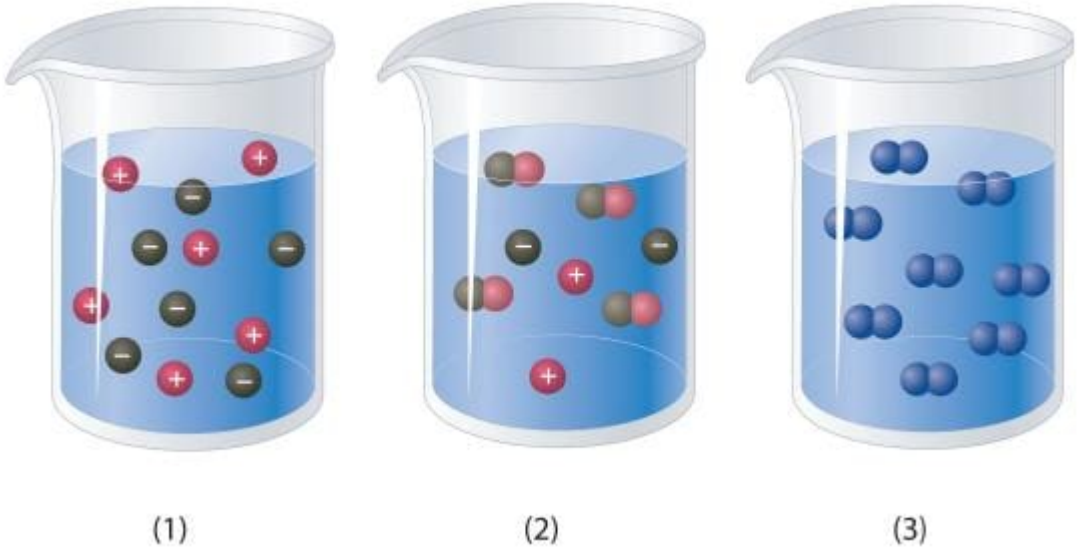
Conceptual Problems

1. Which of the representations best corresponds to a 1 M aqueous solution of each compound? Justify your answers.

   a. NH_3

b. HF
c. $CH_3CH_2CH_2OH$

d. Na_2SO_4



2. Which of the representations shown in Problem 1 best corresponds to a 1 M aqueous solution of each compound? Justify your answers.

   a. CH_3CO_2H
   b. NaCl
   c. Na_2S
   d. Na_3PO_4
   e. acetaldehyde

3. Would you expect a 1.0 M solution of $CaCl_2$ to be a better conductor of electricity than a 1.0 M solution of NaCl? Why or why not?

4. An alternative way to define the concentration of a solution is *molality*, abbreviated *m*. Molality is defined as the number of moles of solute in 1 kg of s*olvent*. How is this different from molarity? Would you expect a 1 M solution of sucrose to be more or less concentrated than a 1 *m* solution of sucrose? Explain your answer.

5. What are the advantages of using solutions for quantitative calculations?

Conceptual Answer

1.

Compound	Corresponding Beaker	Reasoning
NH_3	2	Weak base dissociates into both ions and molecules.
HF	2	Weak acid dissociates into both ions and molecules.
$CH_3CH_2CH_2OH$	3	Covalent compound
Na_2SO_4	1	Soluble ionic compound

2.

CH_3CO_2H	2	Weak acid dissociates into both ions and molecules.
NaCl	1	Soluble ionic compound

Na_2S	1	Soluble ionic compound
Na_3PO_4	1	Soluble ionic compound
Acetaldehyde	1	Aldehydes with short chain lengths are miscible

3. $CaCl_2$ would be expected to be a better conductor than NaCl due to the fact that it contains more charges. The conductivity of a solution depends on the amount of mobile charges within it. While NaCl only has two charges (Na being + and Cl being -), $CaCl_2$ contains three (Ca being 2+ and the two Cls being -). With more free charges when dissolved in the solution, $CaCl_2$ would be a better conductor.
4. Assuming that the solvent is water, the solution with a Molarity (M) of 1 would be more concentrated than the solution with a Molality (m) of 1. Water is approximately 1 kg per liter, meaning that the solute is dissolved in 1 liter of water. This *increases* the amount of solution past 1 liter. Molarity, on the other hand, means that there is 1 liter of solution (that is, including both solute and solvent). Since in both cases there will be one mole, the 1M solution will be more concentrated than the 1m solution because there is less volume, but the same amount of solute.

5. If the amount of a substance required for a reaction is too small to be weighed accurately, the use of a solution of the substance, in which the solute is dispersed in a much larger mass of solvent, allows chemists to measure the quantity of the substance more accurately.

Numerical Problems

1. Calculate the number of grams of solute in 1.000 L of each solution.

    a. 0.2593 M $NaBrO_3$
    b. 1.592 M KNO_3
    c. 1.559 M acetic acid
    d. 0.943 M potassium iodate

2. Calculate the number of grams of solute in 1.000 L of each solution.

    a. 0.1065 M BaI_2
    b. 1.135 M Na_2SO_4
    c. 1.428 M NH_4Br
    d. 0.889 M sodium acetate

3. If all solutions contain the same solute, which solution contains the greater mass of solute?

    a. 1.40 L of a 0.334 M solution or 1.10 L of a 0.420 M solution
    b. 25.0 mL of a 0.134 M solution or 10.0 mL of a 0.295 M solution
    c. 250 mL of a 0.489 M solution or 150 mL of a 0.769 M solution

4. Complete the following table for 500 mL of solution.

Compound	Mass (g)	Moles	Concentration (M)
calcium sulfate	4.86		
acetic acid		3.62	
hydrogen iodide dihydrate			1.273
barium bromide	3.92		
glucose			0.983
sodium acetate		2.42	

5. What is the concentration of each species present in the following aqueous solutions?

a. 0.489 mol of $NiSO_4$ in 600 mL of solution
b. 1.045 mol of magnesium bromide in 500 mL of solution
c. 0.146 mol of glucose in 800 mL of solution
d. 0.479 mol of $CeCl_3$ in 700 mL of solution

6. What is the concentration of each species present in the following aqueous solutions?

a. 0.324 mol of K_2MoO_4 in 250 mL of solution
b. 0.528 mol of potassium formate in 300 mL of solution
c. 0.477 mol of $KClO_3$ in 900 mL of solution
d. 0.378 mol of potassium iodide in 750 mL of solution

7. What is the molar concentration of each solution?

a. 8.7 g of calcium bromide in 250 mL of solution
b. 9.8 g of lithium sulfate in 300 mL of solution
c. 12.4 g of sucrose ($C_{12}H_{22}O_{11}$) in 750 mL of solution
d. 14.2 g of iron(III) nitrate hexahydrate in 300 mL of solution

8. What is the molar concentration of each solution?

a. 12.8 g of sodium hydrogen sulfate in 400 mL of solution
b. 7.5 g of potassium hydrogen phosphate in 250 mL of solution
c. 11.4 g of barium chloride in 350 mL of solution
d. 4.3 g of tartaric acid ($C_4H_6O_6$) in 250 mL of solution

9. Give the concentration of each reactant in the following equations, assuming 20.0 g of each and a solution volume of 250 mL for each reactant.

a. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow$
b. $Ca(OH)_2(aq) + H_3PO_4(aq) \rightarrow$
c. $Al(NO_3)_3(aq) + H_2SO_4(aq) \rightarrow$
d. $Pb(NO_3)_2(aq) + CuSO_4(aq) \rightarrow$
e. $Al(CH_3CO_2)_3(aq) + NaOH(aq) \rightarrow$

10. An experiment required 200.0 mL of a 0.330 M solution of Na_2CrO_4. A stock solution of Na_2CrO_4 containing 20.0% solute by mass with a density of 1.19 g/cm^3 was used to prepare this solution. Describe how to prepare 200.0 mL of a 0.330 M solution of Na_2CrO_4 using the stock solution.

11. Calcium hypochlorite [$Ca(OCl)_2$] is an effective disinfectant for clothing and bedding. If a solution has a $Ca(OCl)_2$ concentration of 3.4 g per 100 mL of solution, what is the molarity of hypochlorite?

12. Phenol (C_6H_5OH) is often used as an antiseptic in mouthwashes and throat lozenges. If a mouthwash has a phenol concentration of 1.5 g per 100 mL of solution, what is the molarity of phenol?

13. If a tablet containing 100 mg of caffeine ($C_8H_{10}N_4O_2$) is dissolved in water to give 10.0 oz of solution, what is the molar concentration of caffeine in the solution?

14. A certain drug label carries instructions to add 10.0 mL of sterile water, stating that each milliliter of the resulting solution will contain 0.500 g of medication. If a patient has a prescribed dose of 900.0 mg, how many milliliters of the solution should be administered?

Numerical Answers

1. Grams of solute in 1.000 L of each solution:

    1. 0.2593 M $NaBrO_3$

1.
2. 1.592 M KNO_3
    1.
3. 1.559 M acetic acid
    1.
4. 0.943 M potassium iodate
    1.
2.
3.
4.

Compound	Mass (g)	Moles	Concentration (M)
calcium sulfate	4.86	0.0357	0.07
acetic acid	217.39	3.62	7.24
hydrogen iodide dihydrate	103.79	0.637	1.273
barium bromide	3.92	0.013	0.026
glucose	88.55	0.491	0.983
sodium acetate	198.52	2.42	4.84

5. Molar Concentration in each solution:
    1. 0.815M $NiSO_4$
    2. 2.09M Magnesium Bromide
    3. 0.183M Glucose
    4. 0.684M $CeCl_3$
6. Molar Concentration in each solution:
    1. 1.296M K_2MoO_4
    2. 1.760M Potassium Formate
    3. 0.530M $KClO_3$
    4. 0.503M Potassium Iodide
7. Molar Concentration in each solution:
    1. 0.174M Calcium Bromide
    2. 0.297M Lithium Sulfate
    3. 0.048M Sucrose
    4. 0.135M Iron(III) Nitrate Hexahydrate
8. Molar Concentration in each solution:
    1. 0.267M Sodium Hydrogen Sulfate
    2. 0.172M Potassium Hydrogen Phosphate
    3. 0.156M Barium Chloride
    4. 0.115M Tartaric Acid
9. Concentration of Reactants in each solution:
    1. 0.192M of $BaCl_2$, 0.282M of Na_2SO_4
    2. 0.541M of $Ca(OH)_2$, 0.408M of H_3PO_4
    3. 0.188M of $Al(NO_3)_3$, 0.408M H_2SO_4(aq)
    4. 0.121M of $Pb(NO_3)_2$, 0.251M $CuSO_4$
    5. 0.196M of $Al(CH_3CO_2)_3$, 1M NaOH
10.
11. 0.4756 M ClO^-
12. 0.159M Phenol
13. 1.74×10^{-3} M caffeine
14. 1.8mL of solution

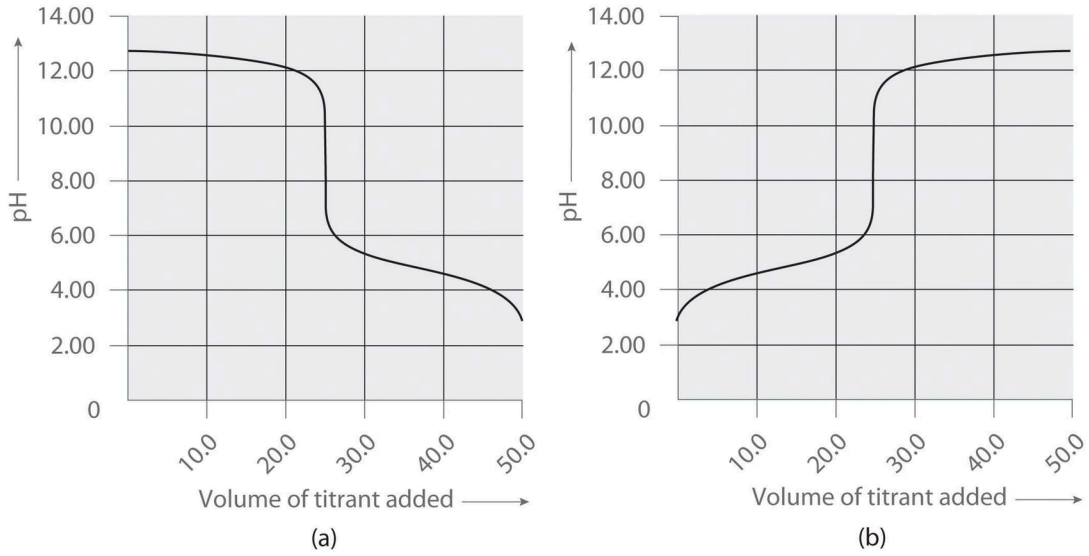
4.6: Solution Stoichiometry and Chemical Analysis

Conceptual Problems

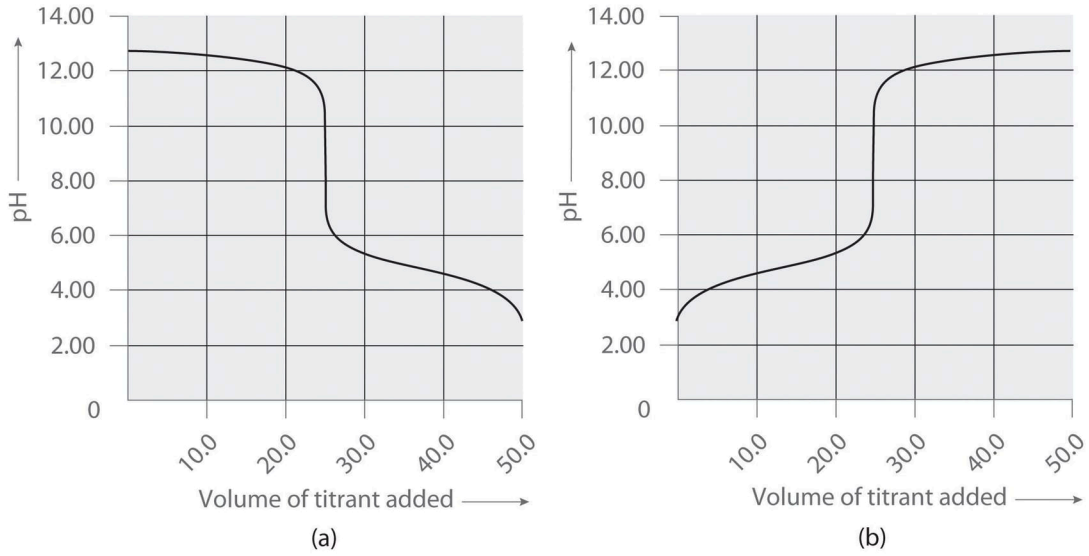
1. The titration procedure is an application of the use of limiting reactants. Explain why this is so.

2. Explain how to determine the concentration of a substance using a titration.

3. Following are two graphs that illustrate how the pH of a solution varies during a titration. One graph corresponds to the titration of 100 mL 0.10 M acetic acid with 0.10 M NaOH, and the other corresponds to the titration of 100 mL 0.10 M NaOH with 0.10 M acetic acid. Which graph corresponds to which titration? Justify your answer.

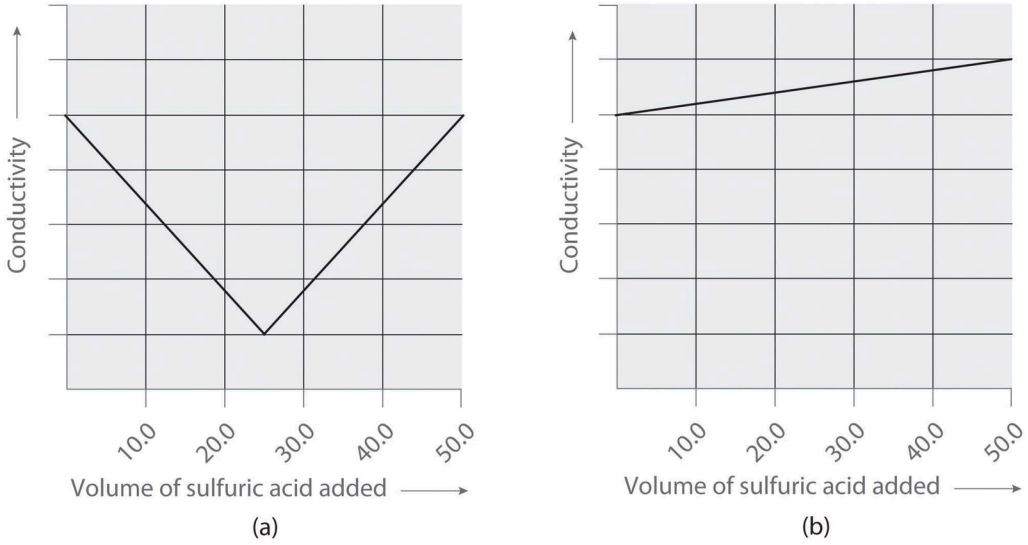


4. Following are two graphs that illustrate how the pH of a solution varies during a titration. One graph corresponds to the titration of 100 mL 0.10 M ammonia with 0.10 M HCl, and the other corresponds to the titration of 100 mL 0.10 M NH_4Cl with 0.10 M NaOH. Which graph corresponds to which titration? Justify your answer.



5. Following are two graphs that illustrate how the electrical conductivity of a solution varies during a titration. One graph

corresponds to the titration of 100 mL 0.10 M $Ba(OH)_2$ with 0.10 M H_2SO_4 , and the other corresponds to the titration of 100 mL of 0.10 M NaOH with 0.10 M H_2SO_4. Which graph corresponds to which titration? Justify your answer.



Conceptual Answers

1. In a titration procedure, the analyte is considered to be the limiting reactant, as the amount of moles of it remain constant while more and more titrant can be added (making the titrant the excess reactant). By using the fact that the analyte is limited, we can continually add the excess reactant to find out just how many moles are in the analyte.
2. To determine the concentration of a solution, one must titrate it with an acid (if the solution is a base) or a base (if the solution is an acid). By titrating the unknown solution with a solution of known concentration, we can determine how many moles of the titrant were needed to fully neutralize the analyte. This point can be determined by finding the *equivalence point* during the titration, and from this knowledge as well as the mole ratio from the balanced neutralization equation, we can determine how many moles are in the analyte. With this, we can simply divide by the original volume to find its concentration.

3. Graph (a) corresponds to the titration of NaOH with acetic acid, while graph (b) corresponds to the titration of acetic acid with NaOH. This can be determined due to our knowledge that acids have a pH below 7 while bases have a pH above 7. Therefore, titrating a base with an acid would decrease its pH while titrating an acid with a base would increase its pH.

4. Graph (a) corresponds to the titration of ammonia with HCl, while graph (b) corresponds to the titration of NH_4Cl with NaOH. This can be determined due to our knowledge that acids have a pH below 7 while bases have a pH above 7. Therefore, titrating a base with an acid would decrease its pH while titrating an acid with a base would increase its pH.
5. 1. titration of $Ba(OH)_2$ with sulfuric acid
   2. titration of NaOH with sulfuric acid

Numerical Problems

1. A 10.00 mL sample of a 1.07 M solution of potassium hydrogen phthalate (KHP, formula mass = 204.22 g/mol) is diluted to 250.0 mL. What is the molarity of the final solution? How many grams of KHP are in the 10.00 mL sample?
2. What volume of a 0.978 M solution of NaOH must be added to 25.0 mL of 0.583 M HCl to completely neutralize the acid? How many moles of NaOH are needed for the neutralization?
3. A student was titrating 25.00 mL of a basic solution with an HCl solution that was 0.281 M. The student ran out of the HCl solution after having added 32.46 mL, so she borrowed an HCl solution that was labeled as 0.317 M. An additional 11.5 mL of the second solution was needed to complete the titration. What was the concentration of the basic solution?

Numerical Answers

1. Final Molarity = 0.0428M, and there are 0.76g of KHP in the initial sample.
2. 15mL of 0.978 M NaOH, or 0.0147 moles.
3. Concentration of basic solution = 0.536 M.

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4.S: Reactions in Aqueous Solution (Summary)

aqueous solutions – solutions in which water is the dissolving medium

4.1: General Properties of Aqueous Solutions

- **electrolyte** – substance whose aqueous solution contains ions
- **nonelectrolyte** – substance that does not form ions in solution

4.2.1 Ionic Compounds in Water

- **dissociate** – when ions separate from a solid being dissolved

4.2.2 Molecular Compounds in Water

- the molecular structure is maintained

4.2.3 Strong and Weak Electrolytes

- strong electrolytes – ionic compounds that exists entirely of ions in solution
- weak electryolytes – molecular compounds that produce a small amound of ions
- chemical equilibrium – equilibrium of forming ions and recrystalizing ions

4.2: Precipitation Reactions

$$AX + BY \rightarrow AY + BX$$

- for methathesis to occur:

    1. the formation of an insoluble product
    2. the formation of either a weak electrolyte or a nonelectrolyte
    3. the formation of a gas that escapes from solution

4.5.1 Precipitation Reactions

- **precipitate** – insoluble solid formed by a reaction in solution
- **solubility** – amount of substance that can be dissolved in a given quantity

4.5.2 Solubility Guidelines for Ionic Compounds

- all common ionic compounds of the alkali metal ions and of the ammonium ion are soluble in water

4.5.3 Reactions in Which a Weak Electrolyte or Nonelectrolyte Forms

- hydrogen and hydroxide react to form water
- insoluble metal oxides react with acids

4.3: Acid-Base Reactions

4.3.1 Acids

- substances that ionize to form hydrogen ions
- proton donors

4.3.2 Bases

- substances that ionize to form hydroxide ions

4.3.3 Strong and Weak Acids and Bases

- **strong acid, strong base** – strong electrolyte
- **weak acid, weak base** – weak electrolyte

4.3.4 Neutralization Reactions and Salts

- **neutralization reaction** – when an acid and base are mixed
- produces water and a salt

4.4 Ionic Equations

- **molecular formula** – and equation written to show the complete chemical formulas of reactants and products
- **spectator ions** – ions that do not play a role in a reaction
- **net ionic equation** – equation where the spectator ions are removed
- only soluble strong electrolytes are written in ionic form

4.4: Oxidation-Reduction Reactions

4.6.1 Reactions in Which a Gas Forms

- carbonates and bicarbonates

4.6.2 Oxidation and Reduction

- **oxidation** – loss of electrons
- **reduction** – gain of electrons

4.6.3 Oxidation of Metals by Acids and Salts

- whenever one substance is oxidized, some other substance must be reduced
- metals react with acids to form salts and hydrogen gas

4.6.4 The Activity Series

- **activity series** – list of metals arranged in order of decreasing ease of oxidation
- **active metals** – alkali metals and alkaline earth metals
- any metal on the list can be oxidized by ions of elements below it

4.5: Concentration of Solutions

- **solution** – homogeneous mixture of two or more substances
- **solvent** – component that is present in greatest quantity
- **solutes** – substances dissolved in the solvent

4.1.1 Molarity

- **concentration** – the amount of solute dissolved in a given quantity of solvent or solution
- **molarity** – number of moles of solute in a liter of solution

Image104.gif

4.1.2 Dilution

- **dilution** - obtaining a lower concentration of a solution by adding water
- moles solute before dilution = moles solute after dilution

Image105.gif

4.6: Solution Stoichiometry and Chemical Analysis

4.7.1 Titrations

- **statndard solution** – solution of known concentration
- **titration** – a known solution that undergoes a specific chemical reaction of known stoichiometry with the solution of unknown concentration
- **equivalence point** – stoichiometrically equivalent quantities of reactants are brought together
- **indicator** – used to show the endpoint of the titration

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5: THERMOCHEMISTRY

This chapter introduces you to **thermochemistry**, a branch of chemistry that describes the energy changes that occur during chemical reactions. In some situations, the energy produced by chemical reactions is actually of greater interest to chemists than the material products of the reaction. For example, the controlled combustion of organic molecules, primarily sugars and fats, within our cells provides the energy for physical activity, thought, and other complex chemical transformations that occur in our bodies. Similarly, our energy-intensive society extracts energy from the combustion of fossil fuels, such as coal, petroleum, and natural gas, to manufacture clothing and furniture, heat your home in winter and cool it in summer, and power the car or bus that gets you to class and to the movies. By the end of this chapter, you will know enough about thermochemistry to explain why ice cubes cool a glass of soda, how instant cold packs and hot packs work, and why swimming pools and waterbeds are heated. You will also understand what factors determine the caloric content of your diet and why even “nonpolluting” uses of fossil fuels may be affecting the environment.

5.1: The Nature of Energy

5.2: The First Law of Thermodynamics

5.3: Enthalpy

5.4: Enthalpy of Reaction

5.5: Calorimetry

5.6: Hess's Law

5.7: Enthalpies of Formation

5.8: Foods and Fuels

5.E: Thermochemistry (Exercises)

5.S: Thermochemistry (Summary)

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5.1: The Nature of Energy

Learning Objectives

- To understand the concept of energy and its various forms.
- To know the relationship between energy, work, and heat.

Because energy takes many forms, only some of which can be seen or felt, it is defined by its effect on matter. For example, microwave ovens produce energy to cook food, but we cannot see that energy. In contrast, we can see the energy produced by a light bulb when we switch on a lamp. In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 5.1.1). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperature of an object is a measure of its thermal energy content. Radiant energy is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energy results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energy is stored in the nucleus of an atom, and chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

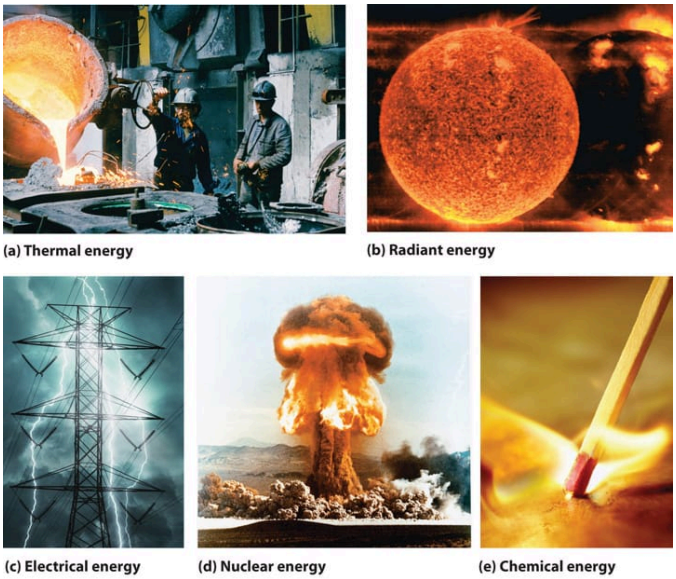


Figure 5.1.1: Forms of Energy. (a) *Thermal energy* results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, which is due to the flow of electrically charged particles. (d) *Nuclear energy* is released when particles in the nucleus of the atom are rearranged. (e) *Chemical energy* results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds.

Electrical energy, nuclear energy, and chemical energy are different forms of potential energy (PE), which is energy stored in an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, kinetic energy (KE) is energy due to the motion of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is then transferred to the object on the ground that it strikes. The electrostatic attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure 5.1.2) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

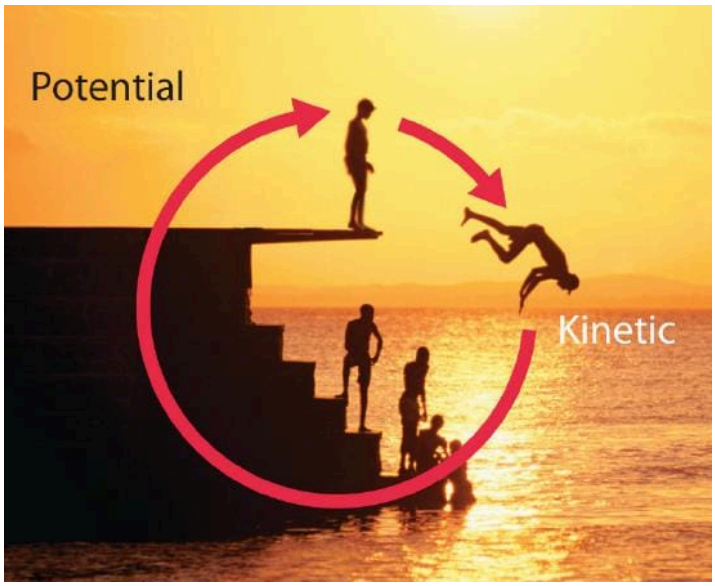


Figure 5.1.2: Interconversion of Forms of Energy. When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the **law of conservation of energy**: *Energy cannot be created or destroyed.*

Energy, Heat, and Work

One definition of energy is the capacity to do work. The easiest form of work to visualize is mechanical work (Figure 5.1.3), which is the energy required to move an object a distance d when opposed by a force F, such as gravity:

work = force x distance

$$w = F\,d \tag{5.1.1}$$

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), we can also write Equation 5.1.1 as follows:

work= mass x acceleration x distance

$$w = m\,a\,d \tag{5.1.2}$$

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth.

Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the force of gravity. The amount of work done (*w*) and thus the energy required depends on three things:

1. the height of the second floor (the distance *d*);
2. your mass, which must be raised that distance against the downward acceleration due to gravity; and
3. your path.

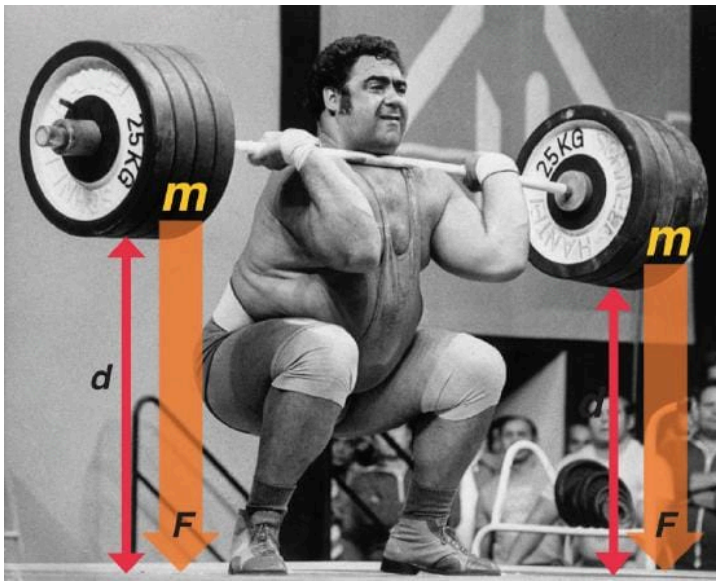


Figure 5.1.2: An Example of Mechanical Work. One form of energy is mechanical work, the energy required to move an object of mass *m* a distance *d* when opposed by a force *F*, such as gravity.

In contrast, heat (*q*) is thermal energy that can be transferred from an object at one temperature to an object at another temperature. The net transfer of thermal energy stops when the two objects reach the same temperature.

Energy is an *extensive* property of matter—for example, the amount of **thermal energy** in an object is proportional to both its mass and its temperature. A water heater that holds 150 L of water at 50°C contains much more thermal energy than does a 1 L pan of water at 50°C. Similarly, a bomb contains much more chemical energy than does a firecracker. We now present a more detailed description of kinetic and potential energy.

Kinetic and Potential Energy

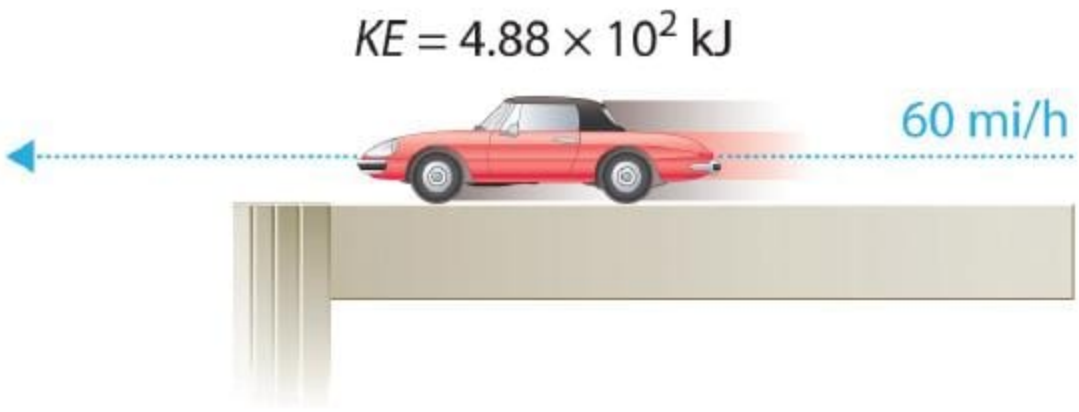
The kinetic energy of an object is related to its mass m and velocity v:

$$KE = \frac{1}{2}mv^2 \tag{5.1.3}$$

For example, the kinetic energy of a 1360 kg (approximately 3000 lb) automobile traveling at a velocity of 26.8 m/s (approximately 60 mi/h) is

$$KE = \frac{1}{2}(1360kg)(26.8ms)^2 = 4.88 \times 10^5 g \cdot m^2 \tag{5.1.4}$$

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J), is named after the British physicist James Joule (1818–1889), an early worker in the field of energy. is defined as 1 kilogram·meter^2/second^2 (kg·m^2/s^2). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10^3 J). For example, the kinetic energy of the 1360 kg car traveling at 26.8 m/s is 4.88 × 10^5 J or 4.88 × 10^2 kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.



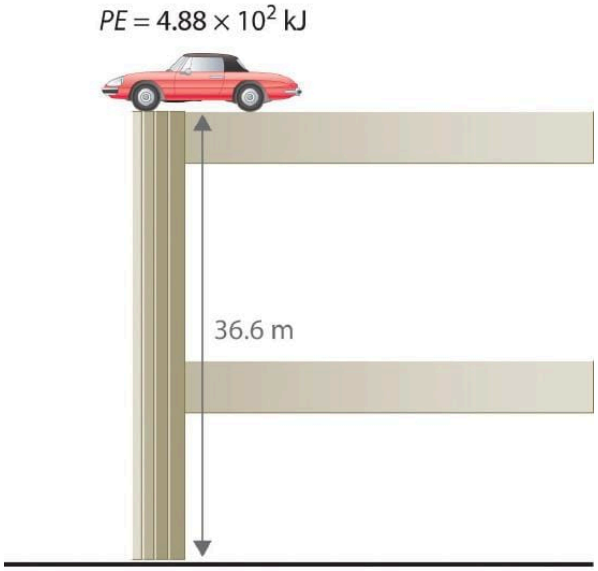
To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is $w = Fd$. According to Equation 5.1.2, the force (F) exerted by gravity on any object is equal to its mass (m, in this case, 1360 kg) times the acceleration (a) due to gravity (g, 9.81 m/s^2 at Earth's surface). The distance (d) is the height (h) above street level (in this case, 36.6 m). Thus the potential energy of the car is as follows:

$$PE = F\,d = m\,a\,d = m\,g\,h \tag{5.1.5}$$

$$PE = (1360, Kg)\left(\frac{9.81\,m}{s^2}\right)(36.6\ m) = 4.88 \times 10^5\ \frac{Kg \cdot m}{s^2} \tag{5.1.6}$$

$$= 4.88 \times 10^5 J = 488\ kJ \tag{5.1.7}$$

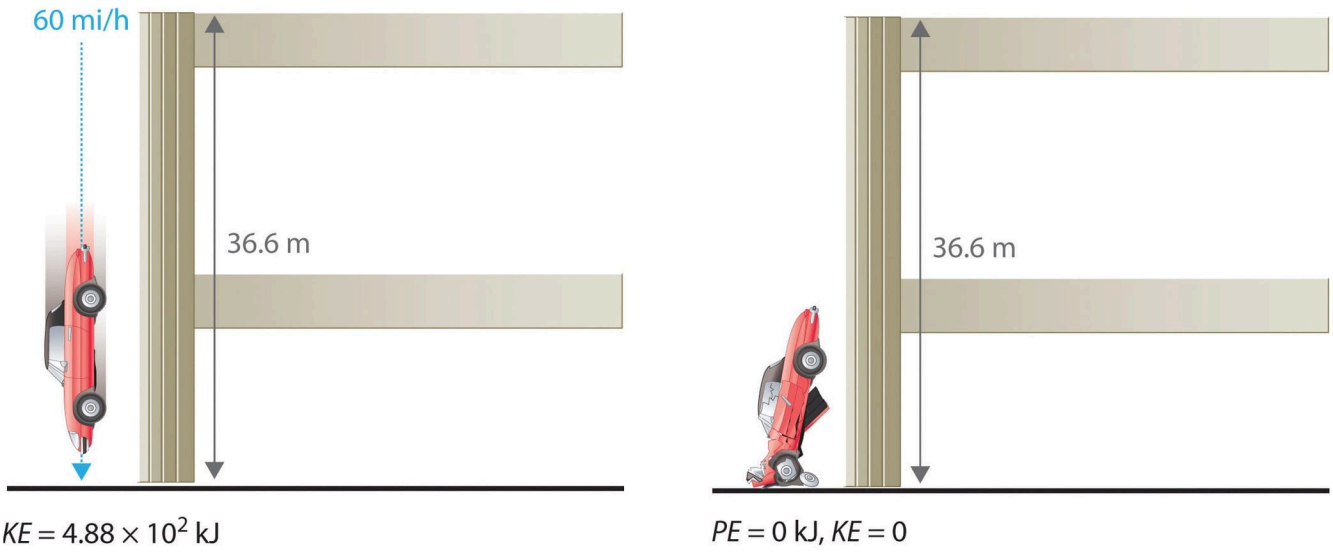
The units of potential energy are the same as the units of kinetic energy. Notice that in this case the potential energy of the stationary automobile at the top of a 36.6 m high parking garage is the same as its kinetic energy at 60 mi/h.



If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic energy would both be zero.

Potential energy is usually defined relative to an arbitrary standard position (in this case, the street was assigned an elevation of zero). As a result, we usually calculate only differences in potential energy: in this case, the difference between the potential energy of the car on the top level of the parking garage and the potential energy of the same car on the street at the base of the

garage.



When the car is falling from the top of the parking structure it has a kinetic energy of 488 kilojoules. When the car hits the floor is has a potential and kinetic energy of zero.

Units of Energy

The units of energy are the same for all forms of energy. Energy can also be expressed in the non-SI units of calories (cal), where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5°C to 15.5°C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1°C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0°C–100°C. The name is derived from the Latin *calor*, meaning "heat." Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$$1\ cal = 4.184\ J \text{ exactly} \tag{5.1.8}$$

$$1\ J = 0.2390\ cal \tag{5.1.9}$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information.

Example 5.1.1

a. If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?
b. A batter hits a pop fly, and the baseball (with a mass of 149 g) reaches an altitude of 250 ft. If we assume that the ball was 3 ft above home plate when hit by the batter, what is the increase in its potential energy?

Given: mass and velocity or height

Asked for: kinetic and potential energy

Strategy:

Use Equation 5.1.4 to calculate the kinetic energy and Equation 5.1.6 to calculate the potential energy, as appropriate.

Solution:

a. The kinetic energy of an object is given by $\frac{1}{2}mv^2$ In this case, we know both the mass and the velocity, but we must convert the velocity to SI units:

$$v = \left(\frac{100\ \cancel{mi}}{1\ \cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.61\ \cancel{km}}{1\ \cancel{mi}}\right)\left(\frac{1000\ m}{1\ \cancel{km}}\right) = 44.7\ m/s$$

The kinetic energy of the baseball is therefore

$$KE = 1492\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{44.7\ m}{s}\right)^2 = 1.49 \times 10^2\ \frac{kg \cdot m^2}{s^2} = 1.49 \times 10^2\ J$$

b. The increase in potential energy is the same as the amount of work required to raise the ball to its new altitude, which is (250 − 3) = 247 feet above its initial position. Thus

$$PE = 149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{9.81\ m}{s^2}\right)(247\ \cancel{ft})\left(\frac{0.3048\ m}{1\ \cancel{ft}}\right) = 1.10 \times 10^2\ \frac{kg \cdot m^2}{s^2} = 1.10 \times 10^2\ J$$

Exercise 5.1.1

a. In a bowling alley, the distance from the foul line to the head pin is 59 ft, 10 13/16 in. (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)
b. What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

Answer a available at the end of this section.

Summary

All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work. *Thermochemistry* is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. **Energy** is the capacity to do work. **Mechanical work** is the amount of energy required to move an object a given distance when opposed by a force. **Thermal energy** is due to the random motions of atoms, molecules, or ions in a substance. The **temperature** of an object is a measure of the amount of thermal energy it contains. **Heat (*q*)** is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of **potential energy (*PE*)**, energy caused by the relative position or orientation of an object. **Kinetic energy (*KE*)** is the energy an object possesses due to its motion. The most common units of energy are the **joule (J)**, defined as 1 (kg·m^2)/s^2, and the **calorie**, defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C (1 cal = 4.184 J).

Answers

Exercise 5.1.1

3.10 × 10^2 J
65 J

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5.2: The First Law of Thermodynamics

Learning Objectives

- To calculate changes in internal energy

To study the flow of energy during a chemical reaction, we need to distinguish between a system, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundings, the rest of the universe, including the container in which the reaction is carried out (Figure 5.2.1). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

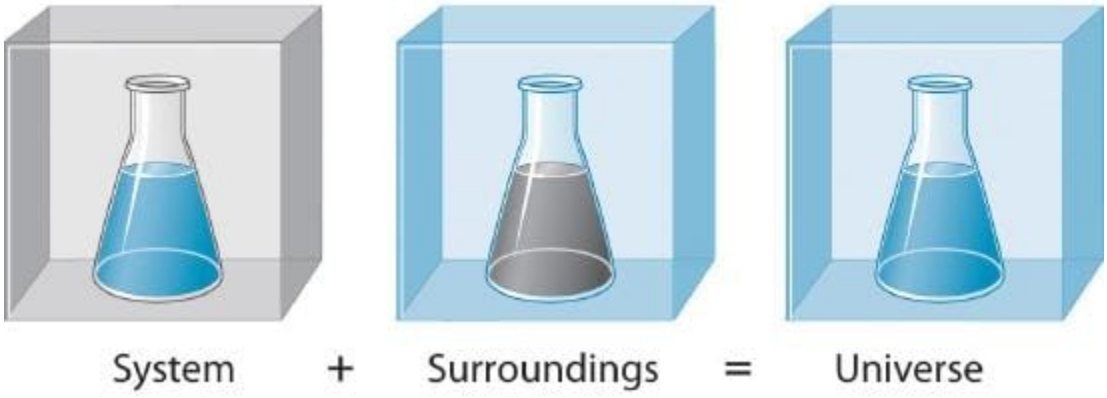


Figure 5.2.1: A System and Its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.

Three kinds of systems are important in chemistry. An **open system** can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A **closed system** can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An **isolated system** exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure 5.2.2). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.

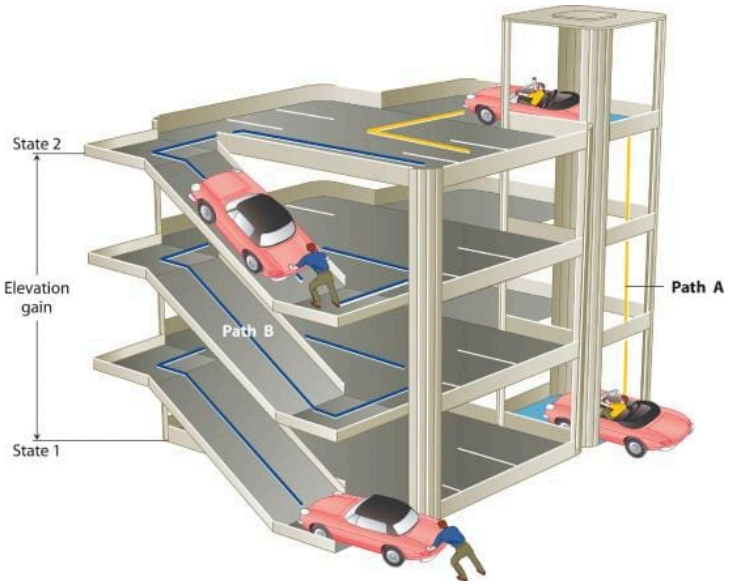


Figure 5.2.2: Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are *not* state functions.

Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (Figure 5.2.3). The balanced chemical equation for the reaction is as follows:

$$2\,\mathrm{Al}\,(\mathrm{s}) + \mathrm{Fe_2O_3}\,(\mathrm{s}) \longrightarrow 2\,\mathrm{Fe}\,(\mathrm{s}) + \mathrm{Al_2O_3}\,(\mathrm{s}) \tag{5.2.1}$$



Figure 5.2.3: The thermite reaction produces so much heat that the iron it produces comes out molten, a property that makes this reaction useful in welding. Image by Kingfisher [CC BY-SA 3.0 (Creative Commons [creativecommons.org])], from Wikimedia Commons.

We can also write this chemical equation as

$$2\,\mathrm{Al}\,(\mathrm{s}) + \mathrm{Fe_2O_3}\,(\mathrm{s}) \;\rightarrow 2\,\mathrm{Fe}\,(\mathrm{s}) + \mathrm{Al_2O_3}\,(\mathrm{s}) + \mathrm{heat} \tag{5.2.2}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including

the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (*q*) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$\text{heat} + \text{H}_2\text{O}\,(\text{s}) \;\rightarrow \text{H}_2\text{O}\,(\text{l}) \tag{5.2.3}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

Heat is technically not a component in Chemical Reactions

Technically, it is poor form to have a $heat$ term in the chemical reaction like in Equations 5.2.2 and 5.2.3 since is it not a true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

The First Law

The relationship between the energy change of a system and that of its surroundings is given by the **first law of thermodynamics**, which states that the energy of the universe is constant. We can express this law mathematically as follows:

$$U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{5.2.4}$$

$$\Delta U_{sys} = -\Delta U_{surr} \tag{5.2.5}$$

where the subscripts univ, sys, and surr refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

> The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane/O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\Delta U_{sys} = q + w \tag{5.2.6}$$

Although q and w are not state functions on their own, their sum (ΔU_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed.

Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

Although q and w are not state functions, their sum (ΔU_{sys}) is independent of the path taken and therefore is a state function.

Thus, because of the first law, we can determine ΔU for any process if we can measure both q and w. Heat, q, may be calculated by measuring a change in temperature of the surroundings. Work, w, may come in different forms, but it too can be measured. One important form of work for chemistry is *pressure-volume work* done by an expanding gas. At a constant external pressure (for example, atmospheric pressure)

$$w = -P\Delta V \tag{5.2.7}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. That is, an expanding gas does work on its surroundings, while a gas that is compressed has work done on it by the surroundings.

Example 5.2.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔU) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A. Determine the sign of q to use in Equation 5.2.6.
B. From Equation 5.2.7 calculate w from the values given. Substitute this value into Equation 5.2.6 to calculate ΔU.

Solution

A From Equation 5.2.6, we know that ΔU = q + w. We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done on the system, so w must be positive. From Equation 5.2.6,

$$w = -P_{\text{ext}}\Delta V = -8.00\text{ atm}(0.0500\text{ L} - 0.400\text{ L})\left(\frac{101.3\text{ J}}{\text{L}\cdot\text{atm}}\right) = 284\text{ J}$$

Thus

$$\begin{aligned}\Delta U &= q + w \\ &= -140\,J + 284\,J \\ &= 144\,J\end{aligned}$$

In this case, although work is done on the gas, increasing its internal energy, heat flows from the system to the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise 5.2.1

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔU) of the gas in joules?

Answer available at the end of this section.

By convention (to chemists), both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**. The first law of thermodynamics states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

Answers

Exercise 5.2.1

–216 J

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5.3: Enthalpy

Learning Objectives

- To know the key features of a state function.
- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Both heat and work represent energy transfer mechanisms. As discussed previously, the term "heat" refers to a *process* in which a body (the contents of a tea kettle, for example) acquires or loses energy as a direct consequence of its having a *different temperature* than its surroundings. Similarly, work refers to the transfer of energy that does not involve temperature differences. Hence, work, like energy, can take various forms, the most familiar being mechanical and electrical.

- *Mechanical work* arises when an object moves a distance Δx against an opposing force f:

$$w_{mechanical} = f\,\Delta x$$

- *Electrical work* is done when a body having a charge q moves through a potential difference ΔV.

$$w_{electrical} = q\Delta V$$

The unit of work is Joules. Work, like heat, exists only when energy is being transferred. When two bodies are placed in thermal contact and energy flows from the warmer body to the cooler one, this process is called "heat". A transfer of energy to or from a system by any means other than heat is called "work".

Enthalpy as a Composite Function

To further understand the relationship between heat flow (q) and the resulting change in internal energy (ΔU), we can look at two sets of limiting conditions: reactions that occur at constant volume and reactions that occur at constant pressure. We will assume that PV work is the only kind of work possible for the system, so we can substitute its definition $w = -P\Delta V$ into the first Law of Thermodynamics ($\Delta U = q + w$) to obtain the following:

$$\Delta U = q - P\Delta V \tag{5.3.1}$$

where the subscripts have been deleted.

If the reaction occurs in a closed vessel, the volume of the system is fixed, and ΔV is zero. Under these conditions, the heat flow (often given the symbol q_v to indicate constant volume) must equal ΔU:

$$\underset{\text{constant volume}}{q_\text{v} = \Delta U} \tag{5.3.2}$$

> At constant volume, no PV work can be done, and the change in the internal energy of the system is equal to the amount of heat transferred from the system to the surroundings or vice versa.

Many chemical reactions are not, however, carried out in sealed containers at constant volume but in open containers at a more or less constant pressure of about 1 atm. The heat flow under these conditions is given the symbol q_p to indicate constant pressure. Replacing q in Equation 5.3.2 by q_p and rearranging to solve for q_p,

$$\underset{\text{constant pressure}}{q_\text{p} = \Delta U + P\Delta V} \tag{5.3.3}$$

Thus, at constant pressure, the heat flow for any process is equal to the change in the internal energy of the system plus the PV work done.

Because conditions of constant pressure are so important in chemistry, a new state function called enthalpy (H) is defined as

$$H = U + PV$$

At constant pressure, the change in the enthalpy of a system is as follows:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V \tag{5.3.4}$$

Comparing the previous two equations shows that at constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$. This expression is consistent with our definition of enthalpy, where we stated that enthalpy is the heat absorbed or produced during any process that occurs at constant pressure.

At constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$.

Example 5.3.1

The molar enthalpy of fusion for ice at 0.0°C and a pressure of 1.00 atm is 6.01 kJ, and the molar volumes of ice and water at 0°C are 0.0197 L and 0.0180 L, respectively. Calculate ΔH and ΔU for the melting of ice at 0.0°C.

Given: enthalpy of fusion for ice, pressure, and molar volumes of ice and water

Asked for: ΔH and ΔU for ice melting at 0.0°C

Strategy:

A. Determine the sign of q and set this value equal to ΔH.
B. Calculate Δ(PV) from the information given.
C. Determine ΔU by substituting the calculated values into Equation 5.3.4.

Solution

A Because 6.01 kJ of heat is absorbed from the surroundings when 1 mol of ice melts, q = +6.01 kJ. When the process is carried out at constant pressure, $q = q_p = \Delta H = 6.01$ kJ.

B To find ΔU using Equation ???, we need to calculate Δ(PV). The process is carried out at a constant pressure of 1.00 atm, so

$$\Delta(PV) = P\Delta V = P(V_f - V) = (1.00\text{ atm})(0.0180\text{ L} - 0.0197\text{ L}) \tag{5.3.5}$$

$$= (-1.7 \times 10^{-3}\text{ L}\cdot\text{atm})(101.3\text{ J/L}\cdot\text{atm}) = -0.0017\text{ J} \tag{5.3.6}$$

C Substituting the calculated values of ΔH and PΔV into Equation 18.11,

$$\Delta U = \Delta H - P\Delta V = 6010\text{ J} - (-0.0017\text{ J}) = 6010\text{ J} = 6.01\text{ kJ}$$

Exercise 5.3.1

At 298 K and 1 atm, the conversion of graphite to diamond requires the input of 1.850 kJ of heat per mole of carbon. The molar volumes of graphite and diamond are 0.00534 L and 0.00342 L, respectively. Calculate ΔH and ΔU for the conversion of C (graphite) to C (diamond) under these conditions.

Answer a available at the end of this section.

The Relationship between ΔH and ΔU

If ΔH for a reaction is known, we can use the change in the enthalpy of the system (Equation 5.3.4) to calculate its change in internal energy. When a reaction involves only solids, liquids, liquid solutions, or any combination of these, the volume does not change appreciably (ΔV = 0). Under these conditions, we can simplify Equation 5.3.4 to ΔH = ΔU. If gases are involved, however, ΔH and ΔU can differ significantly. We can calculate ΔU from the measured value of ΔH by using the right side of Equation 5.3.4 together with the ideal gas law, PV = nRT. Recognizing that Δ(PV) = Δ(nRT), we can rewrite Equation 5.3.4 as follows:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) \tag{5.3.7}$$

At constant temperature, Δ(nRT) = RTΔn, where Δn is the difference between the final and initial numbers of moles of gas. Thus

$$\Delta U = \Delta H - RT\Delta n \tag{5.3.8}$$

For reactions that result in a net production of gas, Δn > 0, so ΔU < ΔH. Conversely, endothermic reactions (ΔH > 0) that result in a net consumption of gas have Δn < 0 and ΔU > ΔH. The relationship between ΔH and ΔU for systems involving gases is illustrated in Example 5.3.2.

> For reactions that result in a net production of gas, ΔU < ΔH. For endothermic reactions that result in a net consumption of gas, ΔU > ΔH.

Example 5.3.2: The Relationship Between ΔH and ΔU in Gas Evolving Reactions

The combustion of graphite to produce carbon dioxide is described by the equation

$$C_{(graphite,s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

At 298 K and 1.0 atm, ΔH = −393.5 kJ/mol of graphite for this reaction, and the molar volume of graphite is 0.0053 L. What is ΔU for the reaction?

Given: balanced chemical equation, temperature, pressure, ΔH, and molar volume of reactant

Asked for: ΔU

Strategy:

A. Use the balanced chemical equation to calculate the change in the number of moles of gas during the reaction.
B. Substitute this value and the data given into Equation 5.3.8 to obtain ΔU.

Solution

A In this reaction, 1 mol of gas (CO_2) is produced, and 1 mol of gas (O_2) is consumed. Thus Δn = 1 − 1 = 0.

B Substituting this calculated value and the given values into Equation 5.3.8,

$$\begin{aligned}\Delta U = \Delta H - RT\Delta n &= (-393.5\text{ kJ/mol}) - [8.314\text{ J/(mol}\cdot\text{K)}](298\text{ K})(0) \\ &= (-393.5\text{ kJ/mol}) - (0\text{ J/mol}) = -393.5\text{ kJ/mol}\end{aligned}$$

To understand why only the change in the volume of the gases needs to be considered, notice that the molar volume of graphite is only 0.0053 L. A change in the number of moles of gas corresponds to a volume change of 22.4 L/mol of gas at standard temperature and pressure (STP), so the volume of gas consumed or produced in this case is (1)(22.4 L) = 22.4 L, which is much, much greater than the volume of 1 mol of a solid such as graphite.

Exercise 5.3.2

Calculate ΔU for the conversion of oxygen gas to ozone at 298 K:

$$3O_2(g) \rightarrow 2O_3(g).$$

The value of ΔH for the reaction is 285.4 kJ.

Answer available at the end of this section.

As Example 5.3.2 illustrates, the magnitudes of ΔH and ΔU for reactions that involve gases are generally rather similar, even when there is a net production or consumption of gases.

Summary

Enthalpy is a state function, and the change in enthalpy of a system is equal to the sum of the change in the internal energy of the system and the PV work done. Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure. The change in the internal energy of a system is the sum of the heat transferred and the work done. At constant pressure, heat flow (q) and internal energy (U) are related to the system's enthalpy (H). The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

Answers

Exercise 5.3.1

ΔH = 1.85 kJ/mol

ΔU = 1.85 kJ/mol

Exercise 5.3.2

288 kJ

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5.4: Enthalpy of Reaction

Learning Objectives

- To understand how enthalpy pertains to chemical reactions

We have stated that the change in energy (ΔU) is equal to the sum of the heat produced and the work performed. Work done by an expanding gas is called *pressure-volume work*, (or just PV *work)*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$\mathrm{Cu\,(s) + 4\,HNO_3\,(aq)\ \rightarrow Cu(NO_3)_2\,(aq) + 2\,H_2O\,(l) + 2\,NO_2\,(g)}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 5.4.1). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of PV work done by multiplying the external pressure P by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure),

$$w = -P\Delta V \tag{5.4.1}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

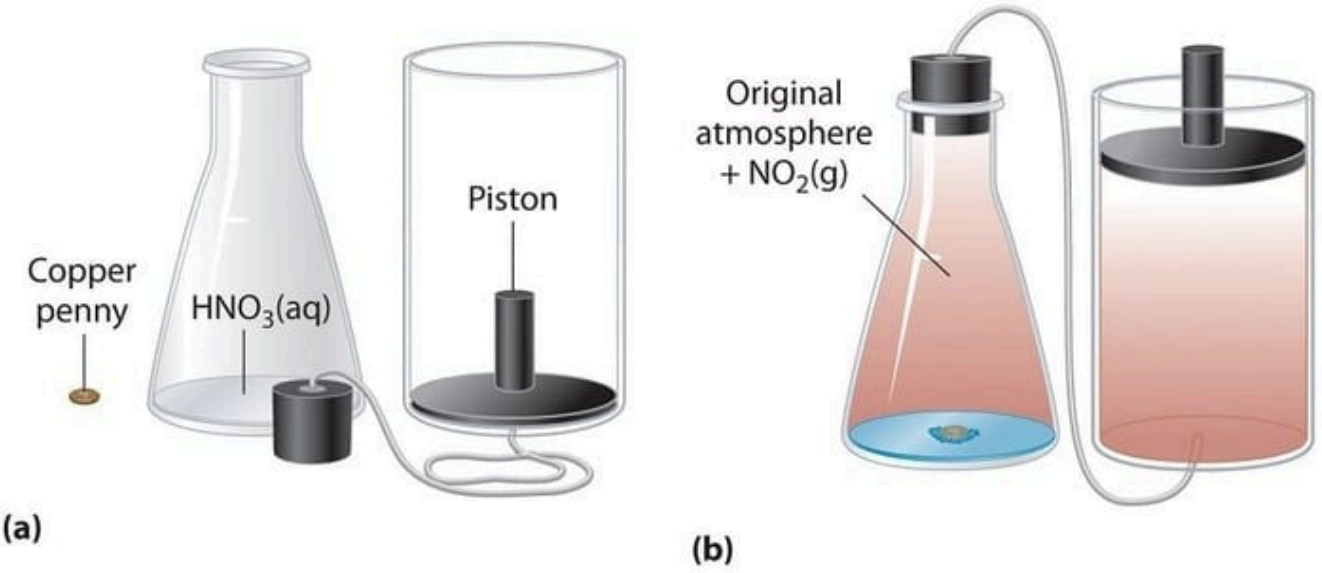


Figure 5.4.1: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings. (CC BY-NC-SA; anonymous)

The internal energy U of a system is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called **enthalpy** (H) (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

\[H =U + PV \label{5.4.3} \]

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function. So we can define a change

in enthalpy (ΔH) accordingly

$$\Delta H = H_{final} - H_{initial}$$

If a chemical change occurs at constant pressure (i.e., for a given P, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) \tag{5.4.2}$$
$$= \Delta U + \Delta PV \tag{5.4.3}$$
$$= \Delta U + P\Delta V \tag{5.4.4}$$

Substituting $q + w$ for ΔU (First Law of Thermodynamics) and $-w$ for $P\Delta V$ (Equation 5.4.1) into Equation 5.4.4, we obtain

$$\Delta H = \Delta U + P\Delta V \tag{5.4.5}$$
$$= q_p + \cancel{w} - \cancel{w} \tag{5.4.6}$$
$$= q_p \tag{5.4.7}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 5.4.7 we see that at constant pressure the change in enthalpy, ΔH of the system, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} \tag{5.4.8}$$
$$= q_p \tag{5.4.9}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

To find ΔH *for a reaction*, measure q_p.

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus:

- $\Delta H_{rxn} < 0$ for an *exothermic reaction*, and
- $\Delta H_{rxn} > 0$ for an *endothermic reaction*.

In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

sign conventions for heat flow and enthalpy changes

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (Figure 5.4.2a). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (Figure 5.4.2b). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

Bond breaking **ALWAYS** requires an input of energy; bond making **ALWAYS** releases energy.y.

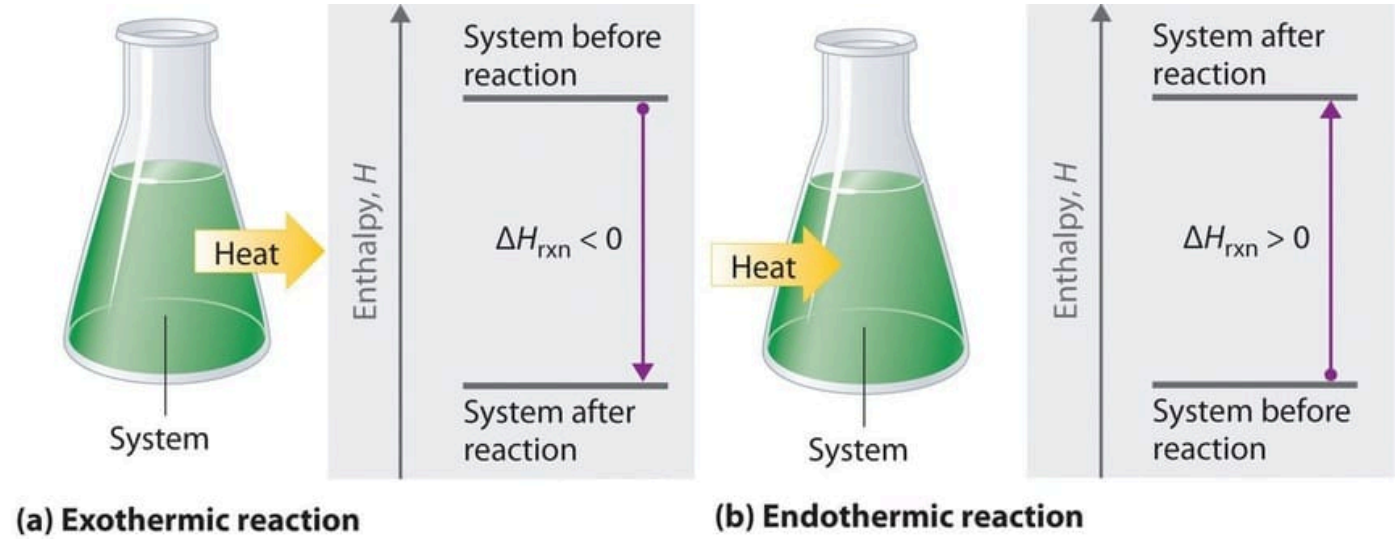


Figure 5.4.2: The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill. (CC BY-NC-SA; anonymous)

- **Reversing a reaction or a process changes the sign of Δ*H*.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$heat + H_2O(s) \rightarrow H_2O(l) \quad \Delta H > 0$$

$$H_2O(l) \rightarrow H_2O(s) + heat \quad \Delta H < 0$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 5.4.10, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

$$2\,\mathrm{Al\,(s)} + \mathrm{Fe_2O_3\,(s)} \longrightarrow 2\,\mathrm{Fe\,(s)} + \mathrm{Al_2O_3\,(s)} + 815.5\ kJ \tag{5.4.10}$$

  Thus ΔH = −851.5 kJ/mol of Fe_2O_3. We can also describe ΔH for the reaction as −425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide −851.5 kJ by 2. When a value for ΔH, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 5.4.11, it is the value of ΔH corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

$$2\,\mathrm{Al\,(s)} + \mathrm{Fe_2O_3\,(s)} \longrightarrow 2\,\mathrm{Fe\,(s)} + \mathrm{Al_2O_3\,(s)} \quad \Delta H_{rxn} = -851.5\ kJ \tag{5.4.11}$$

  If 4 mol of Al and 2 mol of $\mathrm{Fe_2O_3}$ react, the change in enthalpy is 2 × (−851.5 kJ) = −1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{5.4.12}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 5.4.1.

Example 5.4.1: Melting Icebergs

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction at 0°C and constant pressure:

$$\mathrm{H_2O\,(s)} \longrightarrow \mathrm{H_2O\,(l)}$$

How much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A. Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.
B. Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given ΔH for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by ΔH (+6.01 kJ/mol):

$$moles\ H_2O = 1.00 \times 10^6\ \cancel{\text{metric ton}}\ \mathrm{H_2O} \left(\frac{1000\ \cancel{kg}}{1\ \cancel{\text{metric ton}}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right)$$

$$= 5.55 \times 10^{10}\ mol\,\mathrm{H_2O}$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55 \times 10^{10}\ \cancel{mol\ H_2O}\right) = 3.34 \times 10^{11}\ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown below.

Possible sources of the approximately $3.34 \times 10^{11}\ kJ$ needed to melt a 1.00×10^6 metric ton iceberg

- Combustion of 3.8×10^3 ft^3 of natural gas
- Combustion of 68,000 barrels of oil
- Combustion of 15,000 tons of coal
- 1.1×10^8 kilowatt-hours of electricity

Alternatively, we can rely on ambient temperatures to slowly melt the iceberg. The main issue with this idea is the cost of dragging the iceberg to the desired place.

Exercise 5.4.1: Thermite Reaction

If 17.3 g of powdered aluminum are allowed to react with excess $\mathrm{Fe_2O_3}$, how much heat is produced?

Answer available at the end of this section.

Enthalpies of Reaction

One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, since enthalpy is a state function, all we have to know is the initial and final states of the reaction. This allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- Enthalpy of combustion (ΔH_{comb}) The change in enthalpy that occurs during a combustion reaction. Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of fusion (ΔH_{fus}) The enthalpy change that acompanies the melting (fusion) of 1 mol of a substance. The enthalpy change that accompanies the melting, or fusion, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.
- Enthalpy of vaporization (ΔH_{vap}) The enthalpy change that accompanies the vaporization of 1 mol of a substance. The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- Enthalpy of solution (ΔH_{soln}) The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent. The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.

Table 5.4.1: Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points

Substance	ΔH_{vap} (kJ/mol)	ΔH_{fus} (kJ/mol)
argon (Ar)	6.3	1.3
methane (CH_4)	9.2	0.84
ethanol (CH_3CH_2OH)	39.3	7.6
benzene (C_6H_6)	31.0	10.9
water (H_2O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

YouTube Video

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Summary

For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units

of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

Contributors and Attributions

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Answers

Exercise $5.4.1$**: Thermite Reaction**

273 kJ

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5.5: Calorimetry

Learning Objectives

- To use calorimetric data to calculate enthalpy changes.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called *calorimeters*. To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

Heat Capacity

We have seen that the temperature of an object changes when it absorbs or loses thermal energy. The *magnitude* of the temperature change depends on both the *amount* of thermal energy transferred (*q*) and the *heat capacity* of the object. Its heat capacity (*C*) is the amount of energy needed to raise the temperature of the object exactly 1°C; the units of *C* are joules per degree Celsius (J/°C). Note that a degree Celsius is exactly the same as a Kelvin, so the heat capacities can be expresses equally well, and perhaps a bit more correctly in SI, as joules per Kelvin, J/K

The change in temperature (ΔT) is

$$\Delta T = \frac{q}{C} \tag{5.5.1}$$

where *q* is the amount of heat (in joules), *C* is the heat capacity (in joules per degree Celsius), and ΔT is $T_{final} - T_{initial}$ (in degrees Celsius). Note that ΔT is *always* written as the final temperature minus the initial temperature.

Which Temperature units to use

Since the scaling for Kelvin (K) and degrees Celsius (°C) are exactly the same, the DIFFERENCE

$$\Delta T = T_{final} - T_{initial}$$

is the same is either is used for temperature calculations, but make sure not to mix these two temperature units for BOTH T_{final} and $T_{initial}$.

The value of C is intrinsically a positive number, but ΔT and q can be either positive or negative, and they both must have the *same* sign. If ΔT and q are positive, then *heat flows from the surroundings into an object*. If ΔT and q are negative, then *heat flows from an object into its surroundings*.

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity (C_p) is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of C_p are thus J/(mol•°C).The subscript *p* indicates that the value was measured at constant pressure. The specific heat (C_S) is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g•°C).

We can relate the quantity of a substance, the amount of heat transferred, its heat capacity, and the temperature change either via **moles**:

$$q = nC_p\Delta T \tag{5.5.2}$$

where n is the number of moles of substance and C_p is the molar heat capacity or via **mass**:

$$q = mC_s\Delta T \tag{5.5.3}$$

where m is the mass of substance in grams and C_s is the specific heat.

The specific heats of some common substances are given in Table 5.5.1. Note that the specific heat values of most solids are less than 1 J/(g•°C), whereas those of most liquids are about 2 J/(g•°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g•°C), is one of the highest known.

Table 5.5.1: Specific Heats of Selected Substances at 25°C

Compound	Specific Heat [J/(g•°C)]	Compound	Specific Heat [J/(g•°C)]
H_2O (s)	2.108	Al(s)	0.897
H_2O (l)	4.184	Fe(s)	0.449
H_2O (g)	2.062	Cu(s)	0.385
CH_3OH (methanol)	2.531	Au(s)	0.129
CH_3CH_2OH (ethanol)	2.438	Hg(l)	0.140
n-C_6H_{14} (*n*-hexane)	2.270	NaCl(s)	0.864
C_6H_6 (benzene)	1.745	MgO(s)	0.921
C(s) (graphite)	0.709	SiO_2(s) (quartz)	0.742
C(s) (diamond)	0.509	$CaCO_3$(s) (calcite)	0.915

The high specific heat of liquid water has important implications for life on Earth. A given mass of water releases more than five times as much heat for a 1°C temperature change as does the same mass of limestone or granite. Consequently, coastal regions of our planet tend to have less variable climates than regions in the center of a continent. After absorbing large amounts of thermal energy from the sun in summer, the water slowly releases the energy during the winter, thus keeping coastal areas warmer than otherwise would be expected (Figure 5.5.1). Water's capacity to absorb large amounts of energy without undergoing a large increase in temperature also explains why swimming pools and waterbeds are usually heated. Heat must be applied to raise the temperature of the water to a comfortable level for swimming or sleeping and to maintain that level as heat is exchanged with the surroundings. Moreover, because the human body is about 70% water by mass, a great deal of energy is required to change its temperature by even 1 °C. Consequently, the mechanism for maintaining our body temperature at about 37 °C does not have to be as finely tuned as would be necessary if our bodies were primarily composed of a substance with a lower specific heat.

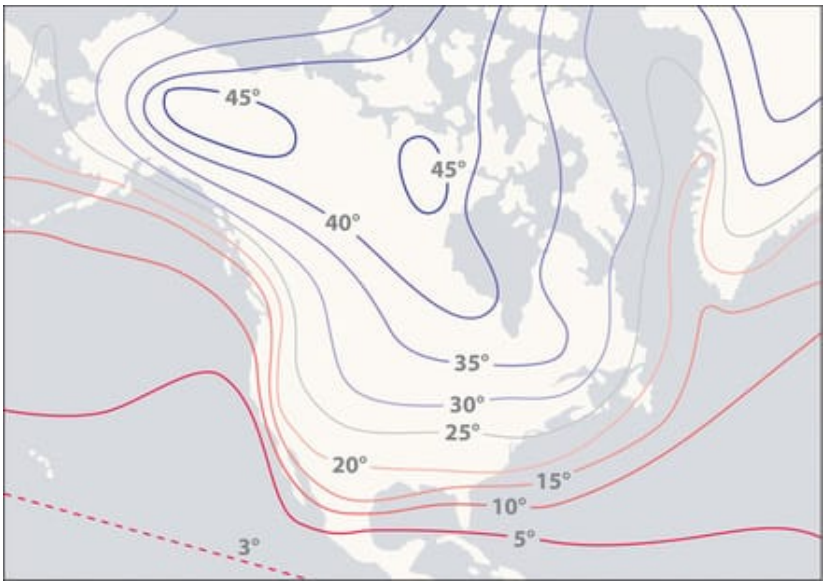


Figure 5.5.1: The High Specific Heat of Liquid Water Has Major Effects on Climate. Regions that are near very large bodies of water, such as oceans or lakes, tend to have smaller temperature differences between summer and winter months than regions in the center of a continent. The contours on this map show the difference between January and July monthly mean surface temperatures (in degrees Celsius).

Example 5.5.1: Solar Heating

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0 °C. During the course of the day, the temperature of the water rises to 38.0 °C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0 °C is 0.998 g/mL.)



Passive solar system. During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A. Use the density of water at 22.0 °C to obtain the mass of water (m) that corresponds to 400 L of water. Then compute ΔT for the water.
B. Determine the amount of heat absorbed by substituting values for m, C_s, and ΔT into Equation 5.5.1.

Solution:

A The mass of water is

$$\text{mass of } H_2O = 400 \cancel{L}\left(\frac{1000\ \cancel{mL}}{1\ \cancel{L}}\right)\left(\frac{0.998\ g}{1\ \cancel{mL}}\right)$$
$$= 3.99 \times 10^5 g\ H_2O$$

The temperature change (ΔT) is

$$38.0^oC - 22.0^oC = +16.0^oC.$$

B From Table 5.5.1, the specific heat of water is 4.184 J/(g•°C). From Equation 5.5.3, the heat absorbed by the water is thus

$$q = mC_s\Delta T$$
$$= \left(3.99 \times 10^5\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)\left(16.0\ \cancel{^oC}\right)$$
$$= 2.67 \times 10^7\ J = 2.67 \times 10^4\ kJ$$

Both q and ΔT are positive, consistent with the fact that the water has absorbed energy.

Exercise 5.5.1: Solar Heating

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 2500 kg of sandstone rocks, what amount of energy is stored if the temperature of the rocks increases from 20.0 °C to 34.5 °C during the day? Assume that the specific heat of sandstone is the same as that of quartz (SiO_2) in Table 5.5.1.

Answer available at the end of this section.

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this process:

$$q_{cold} + q_{hot} = 0 \tag{5.5.4}$$

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

$$q_{cold} = -q_{hot} \tag{5.5.5}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

> Equation 5.5.5 argues that the amount of heat lost by a warmer object equals the amount of heat gained by a cooler object.

Substituting for *q* from Equation 5.5.2 into Equation 5.5.5 gives

$$[mC_s\Delta T]_{cold} + [mC_s\Delta T]_{hot} = 0 \tag{5.5.6}$$

which can be rearranged to give

$$[mC_s\Delta T]_{cold} = -[mC_s\Delta T]_{hot} \tag{5.5.7}$$

When two objects initially at different temperatures are placed in contact, we can use Equation 5.5.7 to calculate the final

temperature if we know the chemical composition and mass of the objects.

Example 5.5.2: Thermal Equilibration of Copper and Water

If a 30.0 g piece of copper pipe at 80.0 °C is placed in 100.0 g of water at 27.0 °C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass and initial temperature of two objects

Asked for: final temperature

Strategy: Using Equation 5.5.6 and writing ΔT as $T_{final} - T_{initial}$ for both the copper and the water, substitute the appropriate values of m, C_s, and $T_{initial}$ into the equation and solve for T_{final}.

Solution

We can adapt Equation 5.5.6 to solve this problem, remembering that ΔT is defined as $T_{final} - T_{initial}$:

$$\left[mC_s\left(T_{final} - T_{initial}\right)\right]_{Cu} + \left[mC_s\left(T_{final} - T_{initial}\right)\right]_{H_2O} = 0$$

Substituting the data provided in the problem and Table 5.5.1 gives

$$\begin{aligned}\left[(30\ g)\,(0.385\ J)\,(T_{final} - 80.0\,^\circ\mathrm{C})\right]_{Cu} + \left[(100\,g)(4.18\,J/\,^\circ\mathrm{C})\,(T_{final} - 27.0\,^\circ\mathrm{C})\right]_{\mathrm{H_2O}} &= 0\\ \left[T_{final}\,(11.6\ J/\,^\circ\mathrm{C}) - 924\ J\right] + \left[T_{final}\,(418.4\ J/\,^\circ\mathrm{C}) - 11,300\ J\right] &= 0\\ T_{final}\,(430\ J/\,(g\cdot\ ^\circ\mathrm{C})) &= 12,224\ J\\ T_{final} &= 28.4\ ^\circ\mathrm{C}\end{aligned}$$

It is expected that the water will increase in temperature since the added copper pipe was hotter. However, the amount of the increase is not great and that is because there is more mass of water (three-fold), but mostly because the greater specific heat of water (order of magnitude) vs. copper.

Exercise 5.5.2A: Thermal Equilibration of Gold and Water

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0 °C, what is the final temperature if no heat is transferred to the surroundings?

Answer available at the end of this section.

Exercise 5.5.2B: Thermal Equilibration of Aluminum and Water

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0 °C. If the final temperature of the water is 24.0 °C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer available at the end of this section.

In Example 5.5.1, radiant energy from the sun was used to raise the temperature of water. A calorimetric experiment uses essentially the same procedure, except that the thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat ($q_{rxn} < 0$), then heat is absorbed by the calorimeter ($q_{calorimeter} > 0$) and its temperature increases. Conversely, if the reaction absorbs heat ($q_{rxn} > 0$), then heat is transferred from the calorimeter to the system ($q_{calorimeter} < 0$) and the temperature of the calorimeter decreases. In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.

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Constant-Pressure Calorimetry

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A "student" version, called a *coffee-cup calorimeter* (Figure $5.5.2$), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C). Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mC_s\Delta T \tag{5.5.8}$$

The use of a constant-pressure calorimeter is illustrated in Example $5.5.3$.

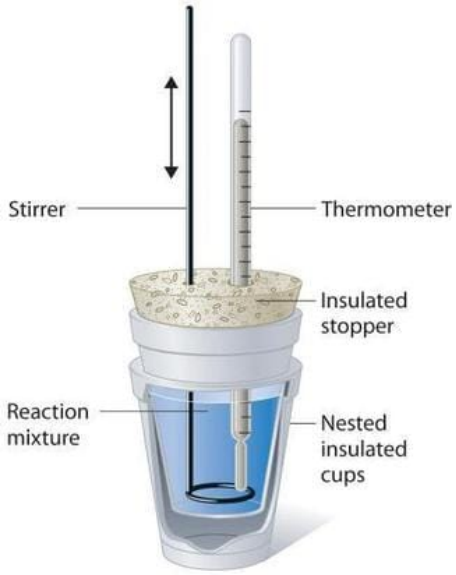


Figure 5.5.2: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

Example 5.5.3: Heat of solution for Potassium Hydroxide

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0 °C to 34.7 °C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A. Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.
B. Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 5.5.8.
C. Use the molar mass of KOH to calculate ΔH_{soln}.

Solution:

A To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$\left(100.0\ \cancel{mL}\ \mathrm{H_2O}\right)\left(0.9969\ g/\cancel{mL}\right) + 5.03\ g\ \mathrm{KOH} = 104.72\ g$$

The temperature change is therefor

$$(34.7\,^oC - 23.0\,^oC) = +11.7\,^oC.$$

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$q_{calorimater} = mC_s\Delta T$$
$$= \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)(11.7\ ^oC)$$
$$= 5130\ J = 5.13\ kJ$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 5.5.1, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\,kJ$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln}, i.e., the heat released when dissolving 1 mol of KOH:

$$\Delta H_{soln} = \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right)$$
$$= -57.2\ kJ/mol$$

Exercise 5.5.3: Heat of solution for ammonium bromide

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7 °C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 5.5.3, find ΔH_{soln} for $\mathrm{NH_4Br}$ (in kilojoules per mole).

Answer available at the end of this section.

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Constant-Volume Calorimetry

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter(A device used to measure energy changes in chemical processes. shown schematically in Figure 5.5.3). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the “bomb”). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

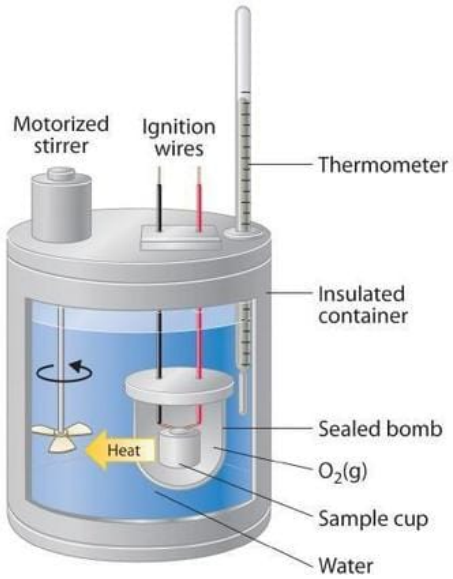


Figure 5.5.3: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.

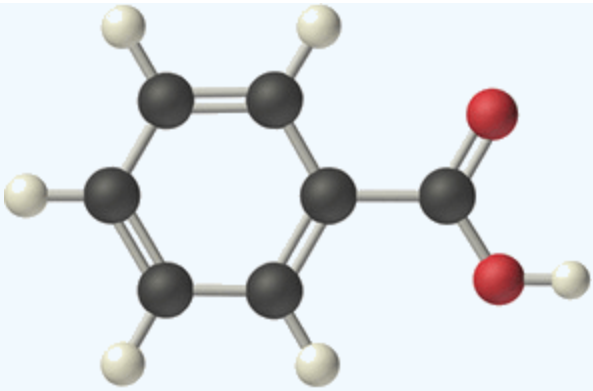
Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔU) rather than the enthalpy change (ΔH); ΔU is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta U < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 5.5.9, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{5.5.9}$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its $\Delta H_{comb} = -26.38\ kJ/g$). This value and the measured increase in temperature of the calorimeter can be used in Equation 5.5.9 to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example 5.5.4.

Example 5.5.4: Combustion of Glucose

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08 °C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Benzoic acid

Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A. Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then use Equation $ref 5.5.9$ to determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.
B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 5.5.9 and the information obtained from the combustion of benzoic acid to calculate C_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$\begin{aligned} q_{comb} &= \left(0.579 \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) \\ &= -15.3\ kJ \end{aligned}$$

From Equation 5.5.9,

$$\begin{aligned} -C_{bomb} &= \frac{q_{comb}}{\Delta T} \\ &= \frac{-15.3\ kJ}{2.08\ ^oC} \\ &= -7.34\ kJ/^oC \end{aligned}$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$\begin{aligned} q_{comb} &= -C_{bomb}\Delta T \\ &= (-7.34\ kJ/^oC)\,(3.64\ ^oC) \\ &= -26.7\ kJ \end{aligned}$$

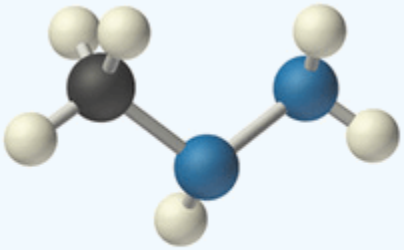
Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\begin{aligned} \Delta H_{comb} &= \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) \\ &= -2780\ kJ/mol \\ &= 2.78 \times 10^3\ J/mol \end{aligned}$$

This result is in good agreement (< 1% error) with the value of $\Delta H_{comb} = -2803\ kJ/mol$ that calculated using enthalpies of formation.

Exercise 5.5.4: Combustion of Benzoic Acid

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75 °C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64 °C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

Answer available at the end of this section.

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Summary

Enthalpy is a state function used to measure the heat transferred from a system to its surroundings or vice versa at constant pressure. Only the **change in enthalpy (Δ*H*)** can be measured. A negative Δ*H* means that heat flows from a system to its surroundings; a positive Δ*H* means that heat flows into a system from its surroundings. Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. **Calorimetry** is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (*C*)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat (C_s)** of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity (C_p)** is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives Δ*H* values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

Answers

Exercise 5.5.1: Solar Heating

$2.7 \times 10^4\ kJ$

Even though the mass of sandstone is more than six times the mass of the water in Example $5.5.1$, the amount of thermal energy stored is the same to two significant figures.

Exercise $5.5.2A$: Thermal Equilibration of Gold and Water

80.0°C

Exercise $5.5.2B$: Thermal Equilibration of Aluminum and Water

90.6°C

Exercise $5.5.3$: Heat of solution for ammonium bromide

16.6 kJ/mol

Exercise $5.5.4$: Combustion of Benzoic Acid

-1.30×10^3 kJ/mol

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5.6: Hess's Law

Learning Objectives

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Because enthalpy is a state function, the enthalpy change for a reaction depends on only two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does not depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

> Hess's Law argues that ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This is nothing more than arguing that ΔH is a state function.

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 5.6.1 can be viewed as occurring in three distinct steps with known ΔH values. As shown in Figure 5.6.1, the first reaction produces 1 mol of solid aluminum oxide (Al_2O_3) and 2 mol of liquid iron at its melting point of 1758°C (part (a) in Equation 5.6.1); the enthalpy change for this reaction is –732.5 kJ/mol of Fe_2O_3. The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (part (b) in Equation 5.6.1); the enthalpy change for this reaction is –13.8 kJ/mol of Fe (–27.6 kJ per 2 mol Fe). In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (part (c) in Equation 5.6.1); the enthalpy change for this reaction is –45.5 kJ/mol of Fe (–91.0 kJ per 2 mol Fe). As you can see in Figure 5.6.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding parts (a), (b), and (c) in Equation 5.6.1 gives the overall reaction, shown in part (d):

$$\begin{aligned}
2\,\mathrm{Al(s,25\,^\circ)} + \mathrm{Fe_2O_3(s,25\,^\circ)} &\longrightarrow 2\,\mathrm{Fe(l,1758\,^\circ)} + \mathrm{Al_2O_3(s,1758\,^\circ)} \qquad \Delta H = -732.5\,\mathrm{kJ} \qquad \text{(a)} \\
2\,\mathrm{Fe(l,1758\,^\circ)} &\longrightarrow 2\,\mathrm{Fe(s,1758\,^\circ)} \qquad \Delta H = -\ 27.6\,\mathrm{kJ} \qquad \text{(b)} \\
2\,\mathrm{Fe(s,1758\,^\circ)} + \mathrm{Al_2O_3(s,1758\,^\circ)} &\longrightarrow 2\,\mathrm{Fe(s,25\,^\circ)} + \mathrm{Al_2O_3(s,25\,^\circ)} \qquad \Delta H = -\ 91.0\,\mathrm{kJ} \qquad \text{(c)} \\
2\,\mathrm{Al(s,25\,^\circ)} + \mathrm{Fe_2O_3(s,25\,^\circ)} &\longrightarrow \mathrm{Al_2O_3(s,25\,^\circ)} + 2\,\mathrm{Fe(s,25\,^\circ)} \qquad \Delta H = -851.1\,\mathrm{kJ} \qquad \text{(d)}
\end{aligned} \tag{5.6.1}$$

The net reaction in part (d) in Equation 5.6.1 is identical to the equation for the thermite reaction that we saw in a previous section. By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 5.6.1.

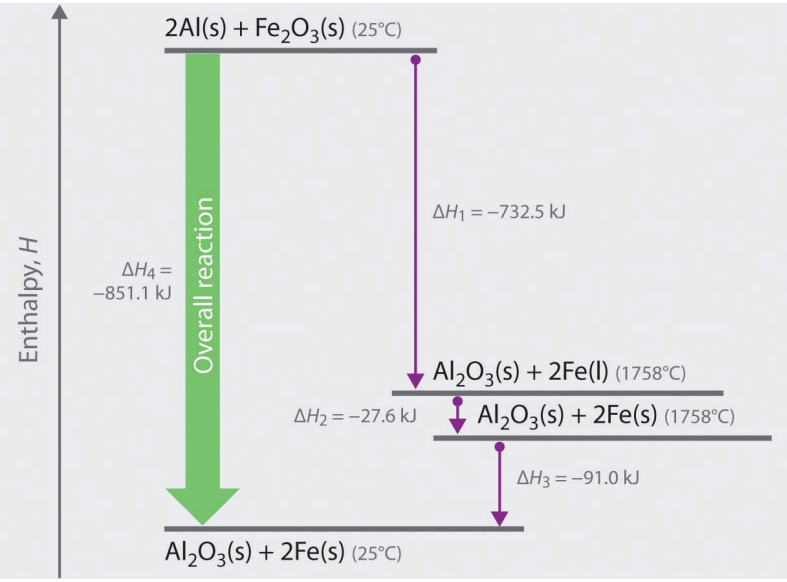


Figure 5.6.1: Energy Changes accompanying the thermite reaction. Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid Al_2O_3 and liquid iron (ΔH_1), solid iron at 1758°C (ΔH_2), and solid iron at 25°C (ΔH_3). Thus $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, as stated by Hess's law.

Comparing parts (a) and (d) in Equation 5.6.1 also illustrates an important point: The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution). When the product is liquid iron at its melting point (part (a) in Equation 5.6.1), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is solid iron at 25°C (part (d) in Equation 5.6.1). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and write individual reactions with known ΔH values that, when added together, will give the desired equation. We illustrate how to use this procedure in Example 5.6.1.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

Example 5.6.1

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

$$(1)\ 2\,C\,(s) + O_2\,(g) \longrightarrow 2\,CO\,(g) \quad \Delta H = -221.0\ kJ$$

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

$$(2)\ C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g) \quad \Delta H = -393.5\ kJ$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2.

Given: two balanced chemical equations and their ΔH values

Asked for: enthalpy change for a third reaction

Strategy:

A. After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH.)
B. Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:

$$(3)\ \mathrm{CO\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(g)} \quad \Delta H_{rxn} = ?$$

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in Equation 3, is a product in Equation 1, we can reverse Equation (1) to give

$$2\,\mathrm{CO\,(g)} \longrightarrow 2\,\mathrm{C\,(s)} + \mathrm{O_2\,(g)} \quad \Delta H = +221.0\ \mathrm{kJ}$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use Equation 2 as written because its product, CO_2, is the product we want in Equation 3:

$$\mathrm{C\,(s)} + \mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(s)} \quad \Delta H = -393.5\ \mathrm{kJ}$$

B Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$2\,\mathrm{C\,(s)} + 2\,\mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(s)} \quad \Delta H = -787.0\ \mathrm{kJ}$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{aligned}
2\,\mathrm{CO\,(g)} &\longrightarrow \cancel{2C(s)} + \cancel{O_2(g)} && \Delta H = -\Delta H_1 = +221.0\ \mathrm{kJ}\\
\cancel{2C(s)} + \cancel{2}\ \mathrm{O_2\,(g)} &\longrightarrow 2\,\mathrm{CO_2\,(g)} && \Delta H = -2\Delta H_2 = -787.0\ \mathrm{kJ}\\
2\,\mathrm{CO\,(g)} + \mathrm{O_2\,(g)} &\longrightarrow 2\,\mathrm{CO_2\,(g)} && \Delta H = -566.0\ \mathrm{kJ}
\end{aligned}$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with O_2, and the problem asks for the amount per mole of CO. Consequently, we must divide both sides of the final equation and the magnitude of ΔH by 2:

$$\mathrm{CO\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(g)} \quad \Delta H = -283.0\ \mathrm{kJ}$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$\begin{aligned}
&(\mathrm{A}) && 2\,\mathrm{C\,(s)} + \mathrm{O_2\,(g)} \longrightarrow \cancel{2CO(g)} && \Delta H_A = \Delta H_1 && = +221.0\ \mathrm{kJ}\\
&(\mathrm{B}) && \cancel{2CO(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(g)} && \Delta H_B && = ?\\
&(\mathrm{C}) && 2\,\mathrm{C\,(s)} + 2\,\mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(g)} && \Delta H = 2\Delta H_2 = 2 \times (-393.5\ \mathrm{kJ}) && = -787.0\ \mathrm{kJ}
\end{aligned}$$

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give CO_2. From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given ΔH for reactions A and C. Substituting the appropriate values gives

$$-221.0\ kJ + \Delta H_B = -787.0\ kJ$$
$$\Delta H_B = -566.0$$

This is again the enthalpy change for the conversion of 2 mol of CO to CO_2. The enthalpy change for the conversion of 1 mol of CO to CO_2 is therefore –566.0 ÷ 2 = –283.0 kJ/mol of CO, which is the same result we obtained earlier. As you can see, there may be more than one correct way to solve a problem.

Exercise 5.6.1

The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$C_2H_2\,(g) + H_2\,(g) \rightarrow C_2H_4\,(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2$$
$$C_2H_2\,(g) + 2H_2\,(g) \rightarrow C_2H_6\,(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2$$

What is ΔH for the reaction of C_2H_4 with H_2 to form C_2H_6?

Answer available at the end of this section.

YouTube Video

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Hess's Law: Hess's Law, YouTube(opens in new window) [youtu.be]

Summary

Hess's law is arguing the overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions. For a chemical reaction, the **enthalpy of reaction (ΔH_{rxn})** is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}. The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion (ΔH_{fus})** and the **enthalpy of vaporization (ΔH_{vap})**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion (ΔH_{comb})** is the enthalpy change that occurs when a substance is burned in excess oxygen.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 5.6.1

–136.3 kJ/mol of C_2H_4

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5.7: Enthalpies of Formation

Learning Objectives

- To understand Enthalpies of Formation and be able to use them to calculate Enthalpies of Reaction

One way to report the heat absorbed or released by chemical reactions would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, starting from the elemental forms of each atom at 25 °C and 1 atm pressure.

Enthalpy of formation (ΔH_f) is the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The formation of any chemical can be as a reaction from the corresponding elements:

$$\text{elements} \rightarrow \text{compound}$$

which in terms of the the Enthalpy of formation becomes

$$\Delta H_{rxn} = \Delta H_f \tag{5.7.1}$$

For example, consider the combustion of carbon:

$$\mathrm{C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)}$$

then

$$\Delta H_{rxn} = \Delta H_f\,[CO_2\,(g)]$$

The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed.

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Standard Enthalpies of Formation

The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The standard conditions for which most thermochemical data are tabulated are a *pressure* of 1 atmosphere (atm) for all gases and a *concentration* of 1 M for all species in solution (1 mol/L). In addition, each pure substance must be in its standard state, which is usually its most stable form at a pressure of 1 atm at a specified temperature. We assume a temperature of 25°C (298 K) for all enthalpy changes given in this text, unless otherwise indicated. Enthalpies of formation measured under these conditions are called **standard enthalpies of formation** (ΔH_f^o) The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition.

> The standard enthalpy of formation of any element in its standard state is zero by definition.

For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), O_2 is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H_2(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure 5.7.1). Therefore, $\mathrm{O_2\,(g)}$, $\mathrm{H_2\,(g)}$, and graphite have ΔH_f^o values of zero.



Figure 5.7.1: Elemental Carbon. Although graphite and diamond are both forms of elemental carbon, graphite is slightly more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H_f^o = -1273.3\ kJ \tag{5.7.2}$$

It is not possible to measure the value of $\Delta H^o o_f$ for glucose, –1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, $\mathrm{O_2}$, and $\mathrm{H_2}$ and measuring the heat evolved as glucose is formed since the reaction shown in Equation 5.7.2 does not occur at a measurable rate under any known conditions. Glucose is not unique; most compounds cannot be prepared by the chemical equations that define their standard enthalpies of formation. Instead, values of $\Delta H^o o_f$ are obtained using **Hess's law** and standard enthalpy changes that have been measured for other reactions, such as combustion reactions. Values of ΔH_f^o for an extensive list of compounds are given in Table T1. Note that ΔH_f^o values are always reported in kilojoules per mole of the substance of interest. Also notice in Table T1 that the standard enthalpy of formation of O_2(g) is zero because it is the most stable form of oxygen in its standard state.

Example 5.7.1: Enthalpy of Formation

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathrm{HCl\,(g)}$
b. $\mathrm{MgCO_3\,(s)}$
c. $\mathrm{CH_3(CH_2)_{14}CO_2H\,(s)}$ (*palmitic acid*)

Given: available at the end of this section.

Exercise 5.7.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathrm{NaCl(s)}$
b. $\mathrm{H_2SO_4(l)}$
c. $\mathrm{CH_3CO_2H(l)}$ (*acetic acid*)

Answer a available at the end of this section.

YouTube Video

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Definition of Heat of Formation Reactions: https://youtu.be/A20k0CK4doI

Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose ΔH_f^o values are known. The standard enthalpy of reaction ΔH_{rxn}^o is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

$$aA + bB \rightarrow cC + dD \tag{5.7.3}$$

where A, B, C, and D are chemical substances and a, b, c, and d are their stoichiometric coefficients. The magnitude of ΔH^o is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

$$\Delta H_{rxn}^o = \underbrace{\left[c\Delta H_f^o(C) + d\Delta H_f^o(D)\right]}_{\text{products}} - \underbrace{\left[a\Delta H_f^o(A) + b\Delta H_f^o(B)\right]}_{\text{reactants}} \tag{5.7.4}$$

More generally, we can write

$$\Delta H_{rxn}^o = \sum m\Delta H_f^o(products) - \sum n\Delta H_f^o(reactants) \tag{5.7.5}$$

where the symbol $\sum$ means "sum of" and m and n are the stoichiometric coefficients of each of the products and the reactants, respectively. "Products minus reactants" summations such as Equation 5.7.5 arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, "products minus reactants" summations are very common in chemistry; we will encounter many others in subsequent chapters.

"Products minus reactants" summations are typical of state functions.

To demonstrate the use of tabulated ΔH^0 values, we will use them to calculate ΔH_{rxn} for the combustion of glucose, the reaction that provides energy for your brain:

$$\mathrm{C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)} \tag{5.7.6}$$

Using Equation 5.7.5, we write

$$\Delta H_f^o = \left\{6\Delta H_f^o\left[CO_2(g)\right] + 6\Delta H_f^o\left[H_2O(g)\right]\right\} - \left\{\Delta H_f^o\left[C_6H_{12}O_6(s)\right] + 6\Delta H_f^o\left[O_2(g)\right]\right\} \tag{5.7.7}$$

From Table T1, the relevant ΔH^0_f values are ΔH^0_f [CO_2(g)] = -393.5 kJ/mol, ΔH^0_f [H_2O(l)] = -285.8 kJ/mol, and ΔH^0_f [$C_6H_{12}O_6$(s)] = -1273.3 kJ/mol. Because O_2(g) is a pure element in its standard state, ΔH^0_f [O_2(g)] = 0 kJ/mol. Inserting these values into

Equation 5.7.7 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\Delta H^o_{comb} = [6\,(-393.5\ kJ/mol) + 6\,(-285.8\ kJ/mol)] - [-1273.3 + 6\,(0\ kJ\ mol)] \tag{5.7.8}$$

$$= -2802.5\ kJ/mol \tag{5.7.9}$$

As illustrated in Figure 5.7.2, we can use Equation 5.7.8 to calculate ΔH^o_f for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH^o_{comb}. The alternative hypothetical pathway consists of **four separate reactions** that convert the reactants to the elements in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH^o_f values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned}
\Delta H^o_1 &= \Delta H^o_f\,[glucose\,(s)] \\
&= -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right) \\
&= +1273.3\ kJ \\
\Delta H^o_2 &= 6\Delta H^o_f\,[O_2\,(g)] \\
&= 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right) \\
&= 0\ kJ
\end{aligned} \tag{5.7.10}$$

Recall that when we reverse a reaction, we must also reverse the **sign** of the accompanying enthalpy change (Equation 5.7.4 since the products are now reactants and vice versa.

The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

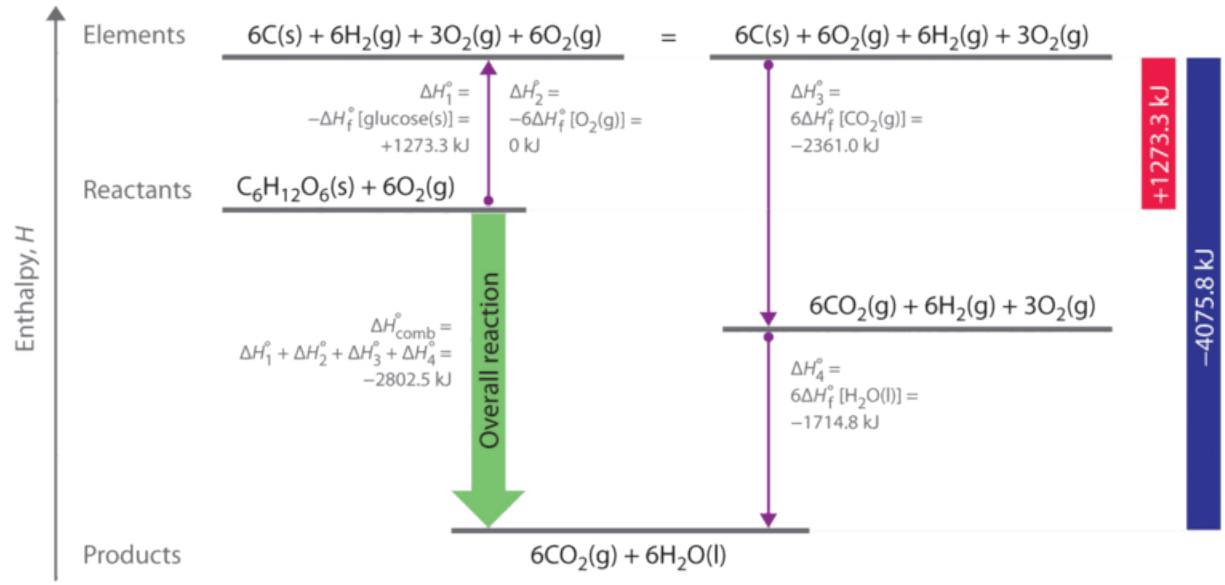


Figure 5.7.1: A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled ΔH^o_1 and ΔH^o_2). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled ΔH^o_3 and ΔH^o_4). Because enthalpy is a state function, ΔH^o_{comb} is equal to the sum of the enthalpy changes $\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$.

The reactions that convert the elements to final products (downward purple arrows in Figure 5.7.2) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes (from Table T1) are

$$\Delta H_3^o = \Delta H_f^o\left[CO_2\left(g\right)\right] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ$$
$$\Delta H_4^o = 6\Delta H_f^o\left[H_2O\left(l\right)\right] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ \tag{5.7.11}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore –4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (–4075.8 kJ):

$$\Delta H_{comb}^o = +1273.3\ kJ + (-4075.8\ kJ) = -2802.5\ kJ \tag{5.7.12}$$

This is the same result we obtained using the "products minus reactants" rule (Equation 5.7.5) and ΔH^0_f values. The two results must be the same because Equation 5.7.12 is just a more compact way of describing the thermochemical cycle shown in Figure 5.7.1.

Example 5.7.2: Heat of Combustion

Long-chain fatty acids such as palmitic acid ($CH_3(CH_2)_{14}CO_2H$) are one of the two major sources of energy in our diet (ΔH_f^o =–891.5 kJ/mol). Use the data in Table T1 to calculate ΔH^0_{comb} for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel — glucose or palmitic acid?

Given: compound and ΔH_f^o values

Asked for: ΔH_{comb}^o per mole and per gram

Strategy:

A. After writing the balanced chemical equation for the reaction, use Equation 5.7.5 and the values from Table T1 to calculate ΔH_{comb}^o the energy released by the combustion of 1 mol of palmitic acid.
B. Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated in Equation 5.7.8 for the combustion of glucose to determine which is the better fuel.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH_f^o. As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_{2(s)} + 23O_{2(g)} \rightarrow 16CO_{2(g)} + 16H_2O_{(l)}$$

Using Equation 5.7.5 ("products minus reactants") with ΔH^0_f values from Table T1 (and omitting the physical states of the reactants and products to save space) gives

$$\begin{aligned}\Delta H_{comb}^o &= \sum m\Delta H_f^o\left(products\right) - \sum n\Delta H_f^o\left(reactants\right)\\ &= \left[16\left(-393.5\ kJ/mol\ CO_2\right) + 16\left(-285.8\ kJ/mol\ H_2O\right)\right]\\ &\quad - \left[-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\left(0\ kJ/mol\ O_2\right)\right]\\ &= -9977.3\ kJ/mol\end{aligned}$$

This is the energy released by the combustion of 1 mol of palmitic acid.

B The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H^o_{comb}\ \ per\ \ gram = \left(\frac{9977.3\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{256.42\ g}\right) = -38.910\ \ kJ/g$$

As calculated in Equation 5.7.8, \(ΔH^o_f\) of glucose is –2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H^o_{comb}\ \ per\ \ gram = \left(\frac{-2802.5\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{180.16\ g}\right) = -15.556\ \ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

Exercise 5.7.2: Water–gas shift reaction

Use Table T1 to calculate ΔH^o_{rxn} for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain H_2(g):

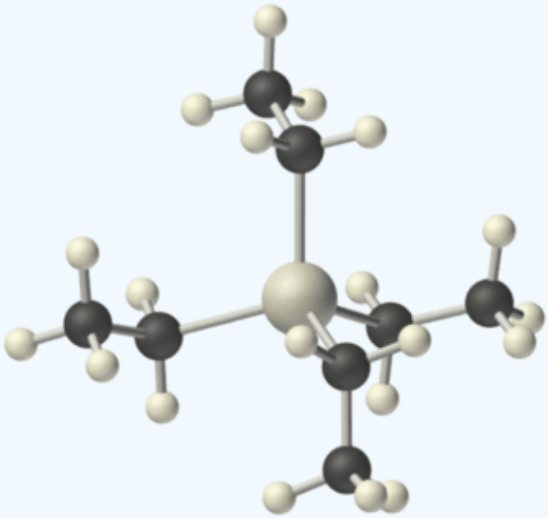
$$\mathrm{CO\ (\ g\ ) + H_2O\ (g\ ) \longrightarrow CO_2\,(g) + H_2\ (\ g\ )}$$

Answer available at the end of this section.

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's ΔH^o_f which we cannot obtain otherwise. This procedure is illustrated in Example 5.7.3.

Example 5.7.3: Tetraethyllead

Beginning in 1923, tetraethyllead [$(C_2H_5)_4Pb$] was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are $\mathrm{CO_2\,(g)}$, $\mathrm{H_2O\,(l)}$, and red $\mathrm{PbO\,(s)}$. What is the standard enthalpy of formation of tetraethyllead, given that ΔH^o_f is –19.29 kJ/g for the combustion of tetraethyllead and ΔH^o_f of red PbO(s) is –219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH^o_{comb} values

Asked for: ΔH_f^o of the reactants

Strategy:

A. Write the balanced chemical equation for the combustion of tetraethyl lead. Then insert the appropriate quantities into Equation 5.7.5 to get the equation for ΔH^0_f of tetraethyl lead.
B. Convert ΔH_{comb}^o per gram given in the problem to ΔH_{comb}^o per mole by multiplying ΔH_{comb}^o per gram by the molar mass of tetraethyllead.
C. Use Table T1 to obtain values of ΔH_f^o for the other reactants and products. Insert these values into the equation for ΔH_f^o of tetraethyl lead and solve the equation.

Solution:

A The balanced chemical equation for the combustion reaction is as follows:

$$2\,(\mathrm{C_2H_5})_4\mathrm{Pb}\,(\mathrm{l}) + 27\,\mathrm{O_2}\,(\mathrm{g}) \longrightarrow 2\,\mathrm{PbO}\,(\mathrm{s}) + 16\,\mathrm{CO_2}\,(\mathrm{g}) + 20\,\mathrm{H_2O}\,(\mathrm{l})$$

Using Equation 5.7.5 gives

$$\Delta H_{comb}^o = \left[2\Delta H_f^o\,(PbO) + 16\Delta H_f^o\,(CO_2) + 20\Delta H_f^o\,(H_2O)\right] - \left[2\Delta H_f^o\,((C_2H_5)_4\,Pb) + 27\Delta H_f^o\,(O_2)\right]$$

Solving for $\Delta H_f^o[(\mathrm{C_2H_5})_4\mathrm{Pb}]$ gives

$$\Delta H_f^o\,((C_2H_5)_4\,Pb) = \Delta H_f^o\,(PbO) + 8\Delta H_f^o\,(CO_2) + 10\Delta H_f^o\,(H_2O) - \frac{27}{2}\Delta H_f^o\,(O_2) - \frac{\Delta H_{comb}^o}{2}$$

The values of all terms other than $\Delta H_f^o[(\mathrm{C_2H_5})_4\mathrm{Pb}]$ are given in Table T1.

B The magnitude of ΔH_{comb}^o is given in the problem in kilojoules per *gram* of tetraethyl lead. We must therefore multiply this value by the molar mass of tetraethyl lead (323.44 g/mol) to get ΔH_{comb}^o for 1 mol of tetraethyl lead:

$$\begin{aligned}\Delta H_{comb}^o &= \left(\frac{-19.29\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right)\\ &= -6329\ kJ/mol\end{aligned}$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, ΔH_{rxn}^o is

$$\begin{aligned}\Delta H_{rxn}^o &= 2\ \cancel{mol\ (C_2H5)_4\,Pb}\left(\frac{-6329\ kJ}{1\ \cancel{mol\ (C_2H5)_4\,Pb}}\right)\\ &= -12,480\ kJ\end{aligned}$$

C Inserting the appropriate values into the equation for $\Delta H_f^o[(\mathrm{C_2H_5})_4\mathrm{Pb}]$ gives

$$\begin{aligned}\Delta H_f^o\,[(C_2H_4)_4\,Pb] &= [1\ mol\ PbO\ \times 219.0\ kJ/mol] + [8\ mol\ CO_2 \times (-393.5\ kJ/mol)] + [10\ mol\ H_2O \times (-285.8\ kJ/mol)] + [-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2]\,[12,480.2\ kJ/mol\ \ (C_2H_5)_4\,Pb]\\ &= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol\end{aligned}$$

Exercise 5.7.3

Ammonium sulfate, $(\mathrm{NH_4})_2\mathrm{SO_4}$, is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$$2\,\mathrm{NH_3}\,(\mathrm{g}) + \mathrm{H_2SO_4}\,(\mathrm{aq}) \ \rightarrow (\mathrm{NH_4})_2\mathrm{SO_4}\,(\mathrm{s})$$

The value of ΔH_{rxn}^o is -179.4 kJ/mole $\mathrm{H_2SO_4}$. Use the data in Table T1 to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer available at the end of this section.

YouTube Video

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Calculating DH° using DHf°: https://youtu.be/Y3aJJno9W2c

Summary

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 °C and 1 atm.
- The elemental form of each atom is that with the lowest enthalpy in the standard state.
- The standard state heat of formation for the elemental form of each atom is zero.

The **enthalpy of formation** (ΔH_f) is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH_f^o) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH_{rxn}^o) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the "products minus reactants" rule. The **enthalpy of solution** (ΔH_{soln}) is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Example $5.7.1$**: Enthalpy of Formation**

compound formula and phase.

balanced chemical equation for its formation from elements in standard states

Use Table T1 to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

To calculate the standard enthalpy of formation of a compound, we must start with the elements in their standard states. The standard state of an element can be identified in Table T1: by a ΔH_f^o value of 0 kJ/mol.

Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $\mathrm{H_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$, respectively, the unbalanced chemical equation is

$$\mathrm{H_2\,(g) + Cl_2\,(g) \;\rightarrow HCl\,(g)}$$

Fractional coefficients are required in this case because ΔH°_f values are reported for *1 mol* of the product, HCl. Multiplying both $\mathrm{H_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$ by 1/2 balances the equation:

$$\mathrm{\tfrac{1}{2}\,H_2\,(g) + \tfrac{1}{2}\,Cl_2\,(g) \;\rightarrow HCl\,(g)}$$

The standard states of the elements in this compound are $\mathrm{Mg\,(s)}$, $\mathrm{C\,(s,\,graphite)}$, and $\mathrm{O_2\,(g)}$. The unbalanced chemical equation is thus

$$\mathrm{Mg\,(s) + C\,(s,\,graphite) + O_2\,(g) \;\rightarrow MgCO_3\,(s)}$$

This equation can be balanced by inspection to give

$$\mathrm{Mg\,(s) + C\,(s,\,graphite) + \tfrac{3}{2}\,O_2\;(g) \rightarrow MgCO_3\,(s)}$$

Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows:

$$\mathrm{C(s, graphite) + H_2(g) + O_2(g) \rightarrow CH_3(CH_2)_{14}CO_2H(s)}$$

There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is

$$\mathrm{16\,C(s, graphite) + 16\,H_2(g) + O_2(g) \longrightarrow CH_3(CH_2)_{14}CO_2H(s)}$$

Exercise 5.7.1

$$\mathrm{Na(s) + \tfrac{1}{2}\,Cl_2(g) \rightarrow NaCl(s)}$$

$$\mathrm{H_2(g) + \tfrac{1}{8}\,S_8(s) + 2\,O_2(\ g) \rightarrow H_2\ SO_4(\ l)}$$

$$\mathrm{2\,C(s) + O_2(g) + 2\,H_2(g) \longrightarrow CH_3CO_2H(l)}$$

Exercise 5.7.2**: Water–gas shift reaction**

–41.2 kJ/mol

Exercise 5.7.3

–1181 kJ/mol

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5.8: Foods and Fuels

Learning Objectives

- To understand the relationship between thermochemistry and nutrition.

The thermochemical quantities that you probably encounter most often are the caloric values of food. Food supplies the raw materials that your body needs to replace cells and the energy that keeps those cells functioning. About 80% of this energy is released as heat to maintain your body temperature at a sustainable level to keep you alive. The nutritional Calorie (with a capital C) that you see on food labels is equal to 1 kcal (kilocalorie). The caloric content of food is determined from its enthalpy of combustion (ΔH_{comb}) per gram, as measured in a bomb calorimeter, using the general reaction

$$\text{food} + \text{excess } \mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} + \mathrm{N_2\,(g)} \tag{5.8.1}$$

There are two important differences, however, between the caloric values reported for foods and the ΔH_{comb} of the same foods burned in a calorimeter. First, the ΔH_{comb} described in joules (or kilojoules) are negative for all substances that can be burned. In contrast, the caloric content of a food is always expressed as a *positive* number because it is *stored energy*. Therefore,

$$\text{caloric content} = -\Delta H_{\text{comb}} \tag{5.8.2}$$

Second, when foods are burned in a calorimeter, any nitrogen they contain (largely from proteins, which are rich in nitrogen) is transformed to N_2. In the body, however, nitrogen from foods is converted to urea [$(H_2N)_2C{=}O$], rather than N_2 before it is excreted. The ΔH_{comb} of urea measured by bomb calorimetry is –632.0 kJ/mol. Consequently, the enthalpy change measured by calorimetry for any nitrogen-containing food is greater than the amount of energy the body would obtain from it. The difference in the values is equal to the ΔH_{comb} of urea multiplied by the number of moles of urea formed when the food is broken down. This point is illustrated schematically in the following equations:

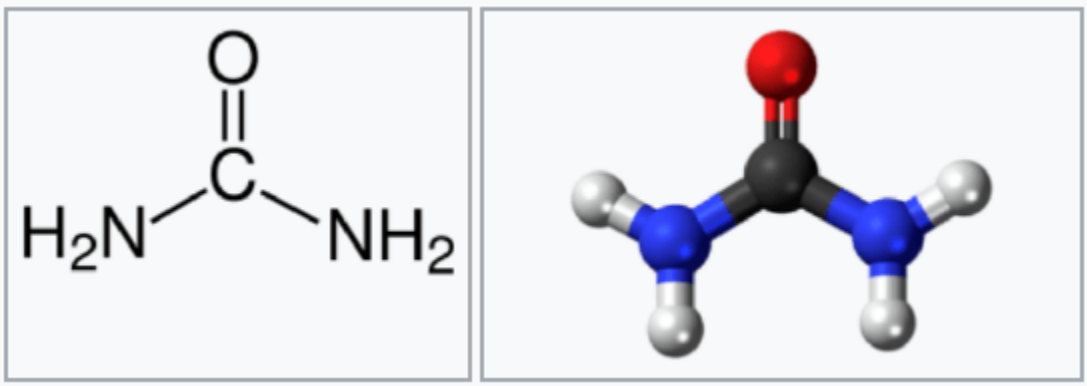
$$\text{food} + \text{excess } \mathrm{O_2\,(g)} \xrightarrow{\Delta H_1 < 0} \mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} + \cancel{(H2N)2C{=}O(s)}$$

$$\cancel{(H2N)2C{=}O(s)} + \tfrac{3}{2}\,\mathrm{O_2\,(g)} \xrightarrow{\Delta H_2 = 632.0\ \text{kJ/mol}} \mathrm{CO_2\,(g)} + 2\,\mathrm{H_2O\,(l)} + \mathrm{N_2\,(g)}$$

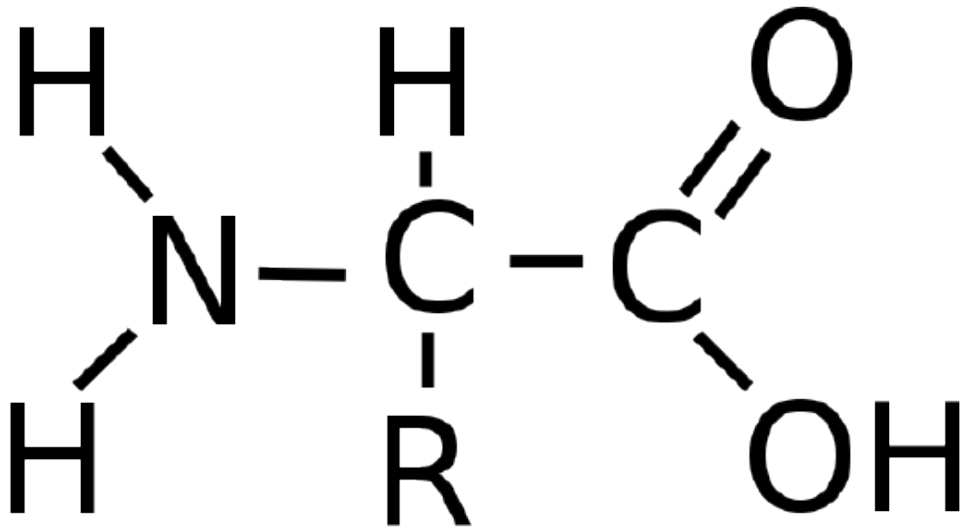
which adds up to

$$\text{food} + \text{excess } \mathrm{O_2\,(g)} \xrightarrow{\Delta H_3 = \Delta H_1 + \Delta H_2 < 0} 2\,\mathrm{CO_2\,(g)} + 3\,\mathrm{H_2O\,(l)} + \mathrm{N_2\,(g)}$$

All three ΔH values are negative, and, by Hess's law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. The magnitude of ΔH_1 must be less than ΔH_3, the calorimetrically measured ΔH_{comb} for a food. By producing urea rather than N_2, therefore, humans are excreting some of the energy that was stored in their food.



Because of their different chemical compositions, foods vary widely in caloric content. As we saw previously, for instance, a fatty acid such as palmitic acid produces about 39 kJ/g during combustion, while a sugar such as glucose produces 15.6 kJ/g. Fatty acids and sugars are the building blocks of fats and carbohydrates, respectively, two of the major sources of energy in the diet. Nutritionists typically assign average values of 38 kJ/g (about 9 Cal/g) and 17 kJ/g (about 4 Cal/g) for fats and carbohydrates, respectively, although the actual values for specific foods vary because of differences in composition. Proteins, the third major source of calories in the diet, vary as well. Proteins are composed of amino acids, which have the following general structure:



General structure of an amino acid. An amino acid contains an amine group ($-NH_2$) and a carboxylic acid group ($-CO_2H$).

In addition to their amine and carboxylic acid components, amino acids may contain a wide range of other functional groups: R can be hydrogen (–H); an alkyl group (e.g., $-CH_3$); an aryl group (e.g., $-CH_2C_6H_5$); or a substituted alkyl group that contains an amine, an alcohol, or a carboxylic acid (Figure 5.8.1). Of the 20 naturally occurring amino acids, 10 are required in the human diet; these 10 are called *essential amino acids* because our bodies are unable to synthesize them from other compounds. Because R can be any of several different groups, each amino acid has a different value of ΔH_{comb}. Proteins are usually estimated to have an average ΔH_{comb} of 17 kJ/g (about 4 Cal/g).

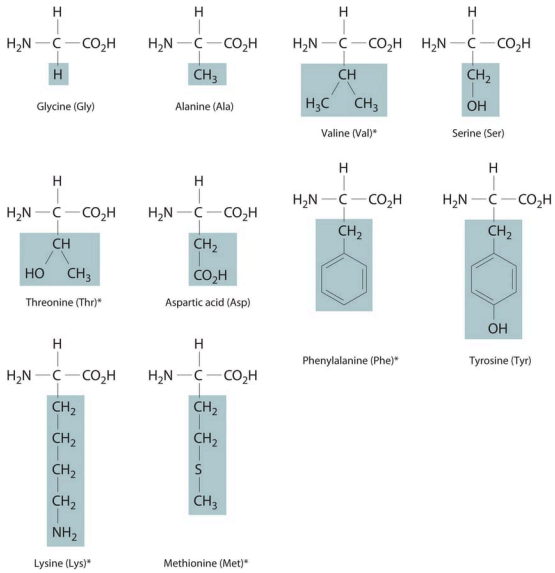
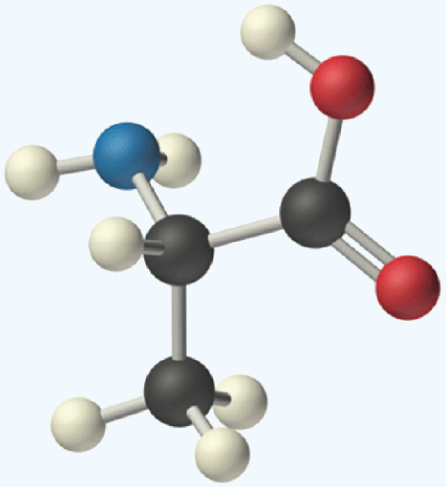


Figure 5.8.1: The Structures of 10 Amino Acids. Essential amino acids in this group are indicated with an asterisk. Structures of glycine, alanine, valine, serine, threonine, aspartic acid, phenylalanine, tyrosine, lysine, methionine.

Example 5.8.1

Calculate the amount of available energy obtained from the biological oxidation of 1.000 g of alanine (an amino acid). Remember that the nitrogen-containing product is urea, not N_2, so biological oxidation of alanine will yield *less* energy than will combustion. The value of ΔH_{comb} for alanine is −1577 kJ/mol.



Alanine

Given: amino acid and ΔH_{comb} per mole

Asked for: caloric content per gram

Strategy:

A. Write balanced chemical equations for the oxidation of alanine to CO_2, H_2O, and urea; the combustion of urea; and the combustion of alanine. Multiply both sides of the equations by appropriate factors and then rearrange them to cancel urea from both sides when the equations are added.

B. Use Hess's law to obtain an expression for ΔH for the oxidation of alanine to urea in terms of the ΔH_{comb} of alanine and urea. Substitute the appropriate values of ΔH_{comb} into the equation and solve for ΔH for the oxidation of alanine to CO_2, H_2O, and urea.
C. Calculate the amount of energy released per gram by dividing the value of ΔH by the molar mass of alanine.

Solution:

The actual energy available biologically from alanine is less than its ΔH_{comb} because of the production of urea rather than N_2. We know the ΔH_{comb} values for alanine and urea, so we can use Hess's law to calculate ΔH for the oxidation of alanine to CO_2, H_2O, and urea.

A We begin by writing balanced chemical equations for (1) the oxidation of alanine to CO_2, H_2O, and urea; (2) the combustion of urea; and (3) the combustion of alanine. Because alanine contains only a single nitrogen atom, whereas urea and N_2 each contain two nitrogen atoms, it is easier to balance Equations 1 and 3 if we write them for the oxidation of 2 mol of alanine:

$$(1)\quad 2C_3H_7NO_2\,(s) + 6O_2\,(g) \rightarrow 5CO_2\,(g) + 5H_2O\,(l) + (H_2N)_2\,C=O\,(s)$$

$$(2)\quad (H_2N)_2\,C=O\,(s) + \frac{3}{2}O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + N_2\,(g)$$

$$(3)\quad (1)\quad 2C_3H_7NO_2\,(s) + \frac{15}{2}O_2\,(g) \rightarrow 6CO_2\,(g) + 7H_2O\,(l) + N_2\,(g)$$

Adding Equations 1 and 2 and canceling urea from both sides give the overall chemical equation directly:

$$(1)\quad 2C_3H_7NO_2\,(s) + 6O_2\,(g) \rightarrow 5CO_2\,(g) + 5H_2O\,(l) + \cancel{(H_2N)_2\,C=O\,(s)}$$

$$\cancel{(2)\quad (H_2N)_2\,C=O\,(s)} + \frac{3}{2}O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + N_2\,(g)$$

$$(3)\quad (1)\quad 2C_3H_7NO_2\,(s) + \frac{15}{2}O_2\,(g) \rightarrow 6CO_2\,(g) + 7H_2O\,(l) + N_2\,(g)$$

B By Hess's law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. We know that $\Delta H_3 = 2\Delta H_{comb}$ (alanine), $\Delta H_2 = \Delta H_{comb}$ (urea), and $\Delta H_1 = 2\Delta H$ (alanine → urea). Rearranging and substituting the appropriate values gives

$$\Delta H_1 = \Delta H_3 - \Delta H_2$$

$$= 2\,(-1577\ kJ/mol) - (-632.0\ kJ/mol)$$

= -2522 \; kJ/\left (2 \;mol\; analine \right) \nonumber \]

Thus ΔH (alanine → urea) = –2522 kJ/(2 mol of alanine) = –1261 kJ/mol of alanine. Oxidation of alanine to urea rather than to nitrogen therefore results in about a 20% decrease in the amount of energy released (–1261 kJ/mol versus –1577 kJ/mol).

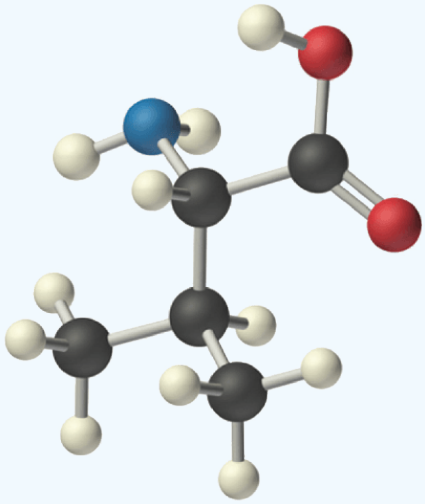
C The energy released per gram by the biological oxidation of alanine is

$$\left(\frac{-1261\ kJ}{1\ \cancel{mol}}\right)\left(\frac{1\ \cancel{mol}}{89.094\ g}\right) = -14.15\ kJ/g$$

This is equal to –3.382 Cal/g.

Exercise 5.8.1

Calculate the energy released per gram from the oxidation of valine (an amino acid) to CO_2, H_2O, and urea. Report your answer to three significant figures. The value of ΔH_{comb} for valine is –2922 kJ/mol.



Valine

Answer available at the end of this section.

The reported caloric content of foods does not include ΔH_{comb} for those components that are not digested, such as fiber. Moreover, meats and fruits are 50%–70% water, which cannot be oxidized by O_2 to obtain energy. So water contains no calories. Some foods contain large amounts of fiber, which is primarily composed of sugars. Although fiber can be burned in a calorimeter just like glucose to give carbon dioxide, water, and heat, humans lack the enzymes needed to break fiber down into smaller molecules that can be oxidized. Hence fiber also does not contribute to the caloric content of food.

Table 5.8.1: Approximate Composition and Fuel Value of an 8 oz Slice of Roast Beef

Composition	Calories
97.5 g of water	× 0 Cal/g = 0
58.7 g of protein	× 4 Cal/g = 235
69.3 g of fat	× 9 Cal/g = 624
0 g of carbohydrates	× 4 Cal/g = 0
1.5 g of minerals	× 0 Cal/g = 0
Total mass: 227.0 g	**Total calories: about 900 Cal**

We can determine the caloric content of foods in two ways. The most precise method is to dry a carefully weighed sample and carry out a combustion reaction in a bomb calorimeter. The more typical approach, however, is to analyze the food for protein, carbohydrate, fat, water, and "minerals" (everything that doesn't burn) and then calculate the caloric content using the average values for each component that produces energy (9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals). An example of this approach is shown in Table 5.8.1 for a slice of roast beef. The compositions and caloric contents of some common foods are given in Table 5.8.2.

Table 5.8.2: Approximate Compositions and Fuel Values of Some Common Foods

Food (quantity)	Approximate Composition (%)				Food Value (Cal/g)	Calories
	Water	Carbohydrate	Protein	Fat		
beer (12 oz)	92	3.6	0.3	0	0.4	150
coffee (6 oz)	100	~0	~0	~0	~0	~0
milk (1 cup)	88	4.5	3.3	3.3	0.6	150

Food (quantity)	Approximate Composition (%)				Food Value (Cal/g)	Calories
egg (1 large)	75	2	12	12	1.6	80
butter (1 tbsp)	16	~0	~0	79	7.1	100
apple (8 oz)	84	15	~0	0.5	0.6	125
bread, white (2 slices)	37	48	8	4	2.6	130
brownie (40 g)	10	55	5	30	4.8	190
hamburger (4 oz)	54	0	24	21	2.9	326
fried chicken (1 drumstick)	53	8.3	22	15	2.7	195
carrots (1 cup)	87	10	1.3	~0	0.4	70

Because the Calorie represents such a large amount of energy, a few of them go a long way. An average 73 kg (160 lb) person needs about 67 Cal/h (1600 Cal/day) to fuel the basic biochemical processes that keep that person alive. This energy is required to maintain body temperature, keep the heart beating, power the muscles used for breathing, carry out chemical reactions in cells, and send the nerve impulses that control those automatic functions. Physical activity increases the amount of energy required but not by as much as many of us hope (Table 5.8.2). A moderately active individual requires about 2500–3000 Cal/day; athletes or others engaged in strenuous activity can burn 4000 Cal/day. Any excess caloric intake is stored by the body for future use, usually in the form of fat, which is the most compact way to store energy. When more energy is needed than the diet supplies, stored fuels are mobilized and oxidized. We usually exhaust the supply of stored carbohydrates before turning to fats, which accounts in part for the popularity of low-carbohydrate diets.

Table 5.8.3: Approximate Energy Expenditure by a 160 lb Person Engaged in Various Activities

Activity	Cal/h
sleeping	80
driving a car	120
standing	140
eating	150
walking 2.5 mph	210
mowing lawn	250
swimming 0.25 mph	300
roller skating	350
tennis	420
bicycling 13 mph	660
running 10 mph	900

Example 5.8.2

What is the minimum number of Calories expended by a 72.6 kg person who climbs a 30-story building? (Assume each flight of stairs is 14 ft high.) How many grams of glucose are required to supply this amount of energy? (The energy released during the combustion of glucose was calculated in Example 5.5.4).

Given: mass, height, and energy released by combustion of glucose

Asked for: calories expended and mass of glucose needed

Strategy:

A. Convert mass and height to SI units and then substitute these values into Equation 5.6 to calculate the change in potential energy (in kilojoules). Divide the calculated energy by 4.184 Cal/kJ to convert the potential energy change to Calories.
B. Use the value obtained in Example 5.5.4 for the combustion of glucose to calculate the mass of glucose needed to supply this amount of energy.

Solution:

The energy needed to climb the stairs equals the difference between the person's potential energy (*PE*) at the top of the building and at ground level.

A Recall that *PE* = *mgh*. Because *m* and *h* are given in non-SI units, we must convert them to kilograms and meters, respectively

$$PE = (72.6\ kg)\left(9.81\ m/s^2\right)(128m) = 8.55 \times 10^4\left(kg \cdot m^2/s^2\right) = 91.2kJ$$

To convert to Calories, we divide by 4.184 kJ/kcal:

$$PE = \left(91.2\ \cancel{kJ}\right)\left(\frac{1\ kcal}{4.184\ \cancel{kJ}}\right) = 21.8\ kcal = 21.8\ Cal$$

B Because the combustion of glucose produces 15.6 kJ/g (Example 5), the mass of glucose needed to supply 85.5 kJ of energy is

$$PE = \left(91.2\ \cancel{kJ}\right)\left(\frac{1\ g\ glucose}{15.6\ \cancel{kJ}}\right) = 5.85\ g\ glucose$$

This mass corresponds to only about a teaspoonful of sugar! Because the body is only about 30% efficient in using the energy in glucose, the actual amount of glucose required would be higher: (100%/30%) × 5.85 g = 19.5 g. Nonetheless, this calculation illustrates the difficulty many people have in trying to lose weight by exercise alone.

Exercise 5.8.2

Calculate how many times a 160 lb person would have to climb the tallest building in the United States, the 110-story Willis Tower in Chicago, to burn off 1.0 lb of stored fat. Assume that each story of the building is 14 ft high and use a calorie content of 9.0 kcal/g of fat.

Answer available at the end of this section.

The calculations in Example 5.8.2 ignore various factors, such as how fast the person is climbing. Although the rate is irrelevant in calculating the change in potential energy, it is very relevant to the amount of energy actually required to ascend the stairs. The calculations also ignore the fact that the body's conversion of chemical energy to mechanical work is significantly less than 100% efficient. According to the average energy expended for various activities listed in Table 5.8.3, a person must run more than 4.5 h at 10 mph or bicycle for 6 h at 13 mph to burn off 1 lb of fat (1.0 lb × 454 g/lb × 9.0 Cal/g = 4100 Cal). But if a person rides a bicycle at 13 mph for only 1 h per day 6 days a week, that person will burn off 50 lb of fat in the course of a year (assuming, of course, the cyclist doesn't increase his or her intake of calories to compensate for the exercise).

Summary

Thermochemical concepts can be applied to determine the actual energy available in food. The nutritional **Calorie** is equivalent to 1 kcal (4.184 kJ). The caloric content of a food is its ΔH_{comb} per gram. The combustion of nitrogen-containing substances produces $N_2(g)$, but the biological oxidation of such substances produces urea. Hence the actual energy available from nitrogen-containing substances, such as proteins, is less than the ΔH_{comb} of urea multiplied by the number of moles of urea produced. The typical caloric contents for food are 9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals.

Answers

Exercise 5.8.1

–22.2 kJ/g (–5.31 Cal/g)

Exercise 5.8.2

About 55 times

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5.E: Thermochemistry (Exercises)

5.1: The Nature of Energy

Conceptual Problems

1. What is the relationship between mechanical work and energy?
2. Does a person with a mass of 50 kg climbing a height of 15 m do work? Explain your answer. Does that same person do work while descending a mountain?
3. If a person exerts a force on an immovable object, does that person do work? Explain your answer.
4. Explain the differences between electrical energy, nuclear energy, and chemical energy.
5. The chapter describes thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy. Which form(s) of energy are represented by each of the following?
    1. sunlight
    2. the energy produced by a cathode ray tube, such as that found in a television
    3. the energy emitted from radioactivity
    4. the energy emitted from a burning candle
    5. the energy associated with a steam engine
    6. the energy emitted by a cellular phone
    7. the energy associated with a stick of dynamite
6. Describe the various forms of energy that are interconverted when a flashlight is switched on.
7. Describe the forms of energy that are interconverted when the space shuttle lifts off.
8. Categorize each of the following as representing kinetic energy or potential energy.
    1. the energy associated with a laptop computer sitting on the edge of a desk
    2. shoveling snow
    3. water pouring out of a fire hydrant
    4. the energy released by an earthquake
    5. the energy in a volcano about to erupt
    6. the energy associated with a coiled spring
9. Are the units for potential energy the same as the units for kinetic energy? Can an absolute value for potential energy be obtained? Explain your answer.
10. Categorize each of the following as representing kinetic energy or potential energy.
    1. water cascading over Niagara Falls
    2. a beaker balanced on the edge of a sink
    3. the energy released during a mudslide
    4. rollerblading
    5. the energy in a block of ice on a rooftop before a thaw
11. Why does hammering a piece of sheet metal cause the metal to heat up?

Conceptual Answers

3. Technically, the person is not doing any work, since the object does not move.

11. The kinetic energy of the hammer is transferred to the metal.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 before proceeding to the Numerical Problems.

1. Describe the mathematical relationship between (a) the thermal energy stored in an object and that object's mass and (b) the thermal energy stored in an object and that object's temperature.

2. How much energy (in kilojoules) is released or stored when each of the following occurs?

    1. A 230 lb football player is lifted to a height of 4.00 ft.
    2. An 11.8 lb cat jumps from a height of 6.50 ft.
    3. A 3.75 lb book falls off of a shelf that is 5.50 ft high.

3. Calculate how much energy (in kilojoules) is released or stored when each of the following occurs:

    1. A 130 lb ice skater is lifted 7.50 ft off the ice.
    2. A 48 lb child jumps from a height of 4.0 ft.
    3. An 18.5 lb light fixture falls from a 10.0 ft ceiling.

4. A car weighing 1438 kg falls off a bridge that is 211 ft high. Ignoring air resistance, how much energy is released when the car hits the water?

5. A 1 tn roller coaster filled with passengers reaches a height of 28 m before accelerating downhill. How much energy is released when the roller coaster reaches the bottom of the hill? Assume no energy is lost due to friction.

Numerical Answers

1.

a. The thermal energy content of an object is directly proportional to its mass.
b. The thermal energy content of an object is directly proportional to its temperature.

3.

a. 1.3 kJ stored
b. 0.26 kJ released
c. 0.251 kJ released

5.

1. 250 kJ released

5.2: The First Law of Thermodynamics

Conceptual Problems

1. Describe how a swinging pendulum that slows with time illustrates the first law of thermodynamics.
2. When air is pumped into a bicycle tire, the air is compressed. Assuming that the volume is constant, express the change in internal energy in terms of q and w.
3. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant pressure?
4. An intrepid scientist placed an unknown salt in a small amount of water. All the salt dissolved in the water, and the temperature of the solution dropped several degrees.

    a. What is the sign of the enthalpy change for this reaction?
    b. Assuming the heat capacity of the solution is the same as that of pure water, how would the scientist calculate the

molar enthalpy change?
c. Propose an explanation for the decrease in temperature.

5. For years, chemists and physicists focused on enthalpy changes as a way to measure the spontaneity of a reaction. What arguments would you use to convince them not to use this method?

6. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant volume?

7. The enthalpy of combustion (ΔH_{comb}) is defined thermodynamically as the enthalpy change for complete oxidation. The complete oxidation of hydrocarbons is represented by the following general equation: hydrocarbon + $O_2(g)$ → $CO_2(g)$ + $H_2O(g)$. Enthalpies of combustion from reactions like this one can be measured experimentally with a high degree of precision. It has been found that the less stable the reactant, the more heat is evolved, so the more negative the value of ΔHcomb. In each pair of hydrocarbons, which member do you expect to have the greater (more negative) heat of combustion? Justify your answers.

   a. cyclopropane or cyclopentane
   b. butane or 2-methylpropane
   c. hexane or cyclohexane

8. Using a structural argument, explain why the trans isomer of 2-butene is more stable than the cis isomer. The enthalpies of formation of cis- and trans-2-butene are –7.1 kJ/mol and –11.4 kJ/mol, respectively.

9. Using structural arguments, explain why cyclopropane has a positive $\Delta H_f°$ (12.7 kJ/mol), whereas cyclopentane has a negative $\Delta H_f°$ (–18.4 kJ/mol). (Hint: consider bond angles.)

Conceptual Answers

3. At constant pressure, ΔH = ΔU + PΔV.
4.

5. In some simple case, when a reaction only involves solids, liquids or liquid solution, we can say that $\Delta H = \Delta U$. When a reaction involves gases, we can say that $\Delta U = \Delta H - RT\Delta n$. However, if we have a complicated case, it is hard to use ΔH to measure the spontaneity of a reaction. For example, when a reaction involved gases, liquid and solid, it is really hard for us to defined $\Delta(PV)$.

9. With bond angles of 60°, cyclopropane is highly strained, causing it to be less stable than cyclopentane, which has nearly ideal tetrahedral geometry at each carbon atom.

Numerical Problems

1. A block of CO_2 weighing 15 g evaporates in a 5.0 L container at 25°C. How much work has been done if the gas is allowed to expand against an external pressure of 0.98 atm under isothermal conditions? The enthalpy of sublimation of CO_2 is 25.1 kJ/mol. What is the change in internal energy (kJ/mol) for the sublimation of CO_2 under these conditions?
2. Zinc and HCl react according to the following equation:

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + H_2(g) \tag{5.E.1}$$

   When 3.00 g of zinc metal is added to a dilute HCl solution at 1.00 atm and 25°C, and this reaction is allowed to go to completion at constant pressure, 6.99 kJ of heat must be removed to return the final solution to its original temperature. What are the values of q and w, and what is the change in internal energy?

3. Acetylene torches, used industrially to cut and weld metals, reach flame temperatures as high as 3000°C. The combustion reaction is as follows:

$$2C_2H_{2\ (g)} + 5O_{2\ (g)} \rightarrow 4CO_{2\ (g)} + 2H_2O_{(l)} \qquad (\Delta H = -2599\ \text{kJ}) \tag{}$$

   Calculate the amount of work done against a pressure of 1.0 atm when 4.0 mol of acetylene are allowed to react with 10 mol of O_2 at 1.0 atm at 20°C. What is the change in internal energy for the reaction?

4. When iron dissolves in 1.00 M aqueous HCl, the products are $FeCl_2(aq)$ and hydrogen gas. Calculate the work done if 30 g of Fe react with excess hydrochloric acid in a closed vessel at 20°C. How much work is done if the reaction takes place in an open vessel with an external pressure of 1.0 atm?

Numerical Answers

1. –350 J; 8.2 kJ

5.3: Enthalpy

5.4: Enthalpy of Reaction

Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Conceptual Problems.

1. Heat implies the flow of energy from one object to another. Describe the energy flow in an

   a. exothermic reaction.

   b. endothermic reaction.

2. When a thermometer is suspended in an insulated thermos that contains a block of ice, the temperature recorded on the thermometer drops. Describe the direction of heat flow.

3. In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. State whether each process is endothermic or exothermic.

   1. Water is added to sodium hydroxide pellets, and the flask becomes hot.
   2. The body metabolizes glucose, producing carbon dioxide and water.
   3. Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.

4. In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. Determine whether each process is endothermic or exothermic.

   1. Concentrated acid is added to water in a flask, and the flask becomes warm.
   2. Water evaporates from your skin, causing you to shiver.
   3. A container of ammonium nitrate detonates.

5. Is Earth's environment an isolated system, an open system, or a closed system? Explain your answer.

6. Why is it impossible to measure the absolute magnitude of the enthalpy of an object or a compound?

7. Determine whether energy is consumed or released in each scenario. Explain your reasoning.

   1. A leaf falls from a tree.
   2. A motorboat maneuvers against a current.
   3. A child jumps rope.
   4. Dynamite detonates.
   5. A jogger sprints down a hill.

8. The chapter states that enthalpy is an extensive property. Why? Describe a situation that illustrates this fact.

9. The enthalpy of a system is affected by the physical states of the reactants and the products. Explain why.

10. Is the distance a person travels on a trip a state function? Why or why not?

5.5: Calorimetry

Conceptual Problems

1. Can an object have a negative heat capacity? Why or why not?
2. What two factors determine the heat capacity of an object? Does the specific heat also depend on these two factors? Explain your answer.
3. Explain why regions along seacoasts have a more moderate climate than inland regions do.
4. Although soapstone is more expensive than brick, soapstone is frequently the building material of choice for fireplaces, particularly in northern climates with harsh winters. Propose an explanation for this.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Numerical Problems.

1. Using Equation 9.6.2 and Equation 9.6.3, derive a mathematical relationship between C_s and C_p.

2. Complete the following table for 28.0 g of each element at an initial temperature of 22.0°C.

Element	q (J)	C_p [J/(mol·K)]	Final T (°C)
nickel	137	26.07	
silicon		19.789	3.0
zinc	603		77.5
mercury	137		57

3. Using Table 9.6.1, how much heat is needed to raise the temperature of a 2.5 g piece of copper wire from 20°C to 80°C? How much heat is needed to increase the temperature of an equivalent mass of aluminum by the same amount? If you were using one of these metals to channel heat away from electrical components, which metal would you use? Once heated, which metal will cool faster? Give the specific heat for each metal.

4. Gold has a molar heat capacity of 25.418 J/(mol·K), and silver has a molar heat capacity of 23.350 J/(mol·K).

    1. If you put silver and gold spoons of equal mass into a cup of hot liquid and wait until the temperature of the liquid is constant, which spoon will take longer to cool down when removed from the hot liquid?
    2. If 8.00 g spoons of each metal at 20.0°C are placed in an insulated mug with 50.0 g of water at 97.0°C, what will be the final temperature of the water after the system has equilibrated? (Assume that no heat is transferred to the surroundings.)

5. In an exothermic reaction, how much heat would need to be evolved to raise the temperature of 150 mL of water 7.5°C? Explain how this process illustrates the law of conservation of energy.

6. How much heat must be evolved by a reaction to raise the temperature of 8.0 oz of water 5.0°C? What mass of lithium iodide would need to be dissolved in this volume of water to produce this temperature change?

7. A solution is made by dissolving 3.35 g of an unknown salt in 150 mL of water, and the temperature of the water rises 3.0°C. The addition of a silver nitrate solution results in a precipitate. Assuming that the heat capacity of the solution is the same as that of pure water, use the information in Table 9.5.1 and solubility rules to identify the salt.

8. Using the data in Table 9.8.2, calculate the change in temperature of a calorimeter with a heat capacity of 1.78 kJ/°C when 3.0 g of charcoal is burned in the calorimeter. If the calorimeter is in a 2 L bath of water at an initial temperature of 21.5°C, what will be the final temperature of the water after the combustion reaction (assuming no heat is lost to the surroundings)?

9. A 3.000 g sample of TNT (trinitrotoluene, $C_7H_5N_3O_6$) is placed in a bomb calorimeter with a heat capacity of 1.93 kJ/°C; the ΔH_{comb} of TNT is −3403.5 kJ/mol. If the initial temperature of the calorimeter is 19.8°C, what will be the final temperature of the calorimeter after the combustion reaction (assuming no heat is lost to the surroundings)? What is the ΔH_f of TNT?

Answers

1. $C_p = C_s \times$ (molar mass)
2.
3. For Cu: q = 58 J; For Al: q = 130 J; Even though the values of the molar heat capacities are very similar for the two metals, the specific heat of Cu is only about half as large as that of Al, due to the greater molar mass of Cu versus Al: C_s = 0.385 and 0.897 *J*/(g•K) for Cu and Al, respectively. Thus loss of one joule of heat will cause almost twice as large a decrease in temperature of Cu versus Al.
4.
5. 4.7 kJ
6.
7. ΔH_{soln} = −0.56 kJ/g; based on reaction with $AgNO_3$, salt contains halide; dividing ΔH_{soln} values in Table 5.2 by molar mass of salts gives lithium bromide as best match, with −0.56 kJ/g.
8.
9. T_{final} = 43.1°C; the combustion reaction is

$$4C_7H_5N_3O_{6(s)} + 21O_{2(g)} \rightarrow 28CO_{2(g)} + 10H_2O_{(g)} + 6N_{2(g)} \tag{5.E.2}$$

with

$$\Delta^o_f H(TNT) = -65.5\ kJ/mol \tag{5.E.3}$$

5.6: Hess's Law

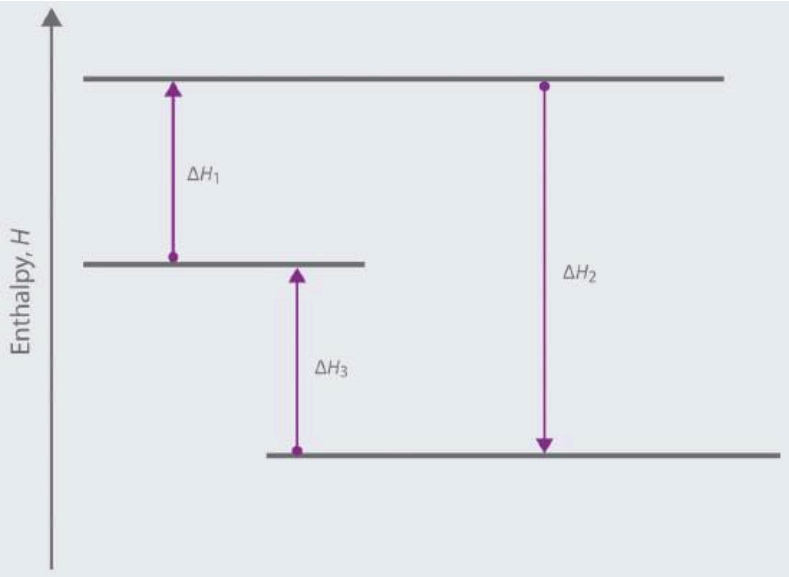
Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Conceptual Problems.

1. Based on the following energy diagram,

   a. write an equation showing how the value of ΔH_2 could be determined if the values of ΔH_1 and ΔH_3 are known.

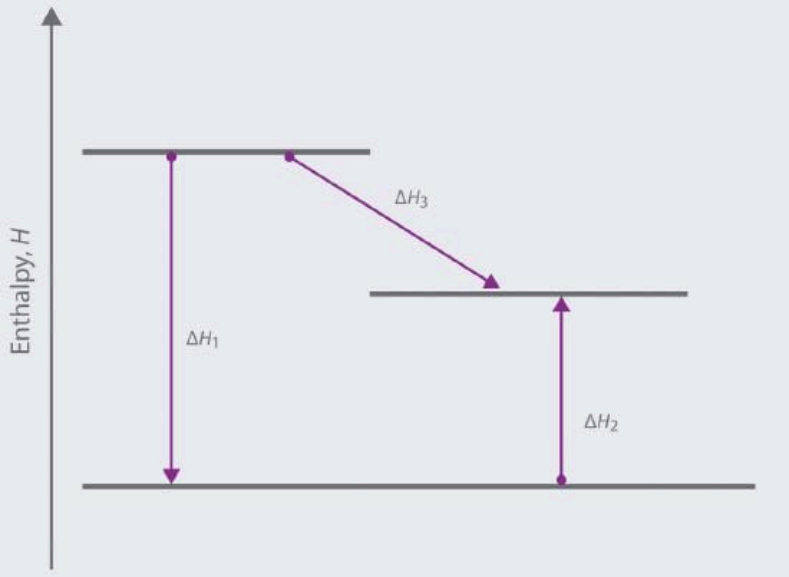
   b. identify each step as being exothermic or endothermic.



2. Based on the following energy diagram,

   a. write an equation showing how the value of ΔH_3 could be determined if the values of ΔH_1 and ΔH_2 are known.

   b. identify each step as being exothermic or endothermic.



3. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.

4. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?

   1. the melting of a solid
   2. the conversion of a gas to a liquid
   3. the solidification of a liquid
   4. the dissolution of a solid into water

5. In their elemental form, A_2 and B_2 exist as diatomic molecules. Given the following reactions, each with an associated $\Delta H°$, describe how you would calculate ΔH^{o}_{f} for the compound AB_2.

$$\begin{array}{lcll} 2AB & \rightarrow & A_2 + B_2 & \Delta H_1^o \\ 3AB & \rightarrow & AB_2 + A_2B & \Delta H_2^o \\ 2A_2B & \rightarrow & 2A_2 + B_2 & \Delta H_3^o \end{array}$$

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 before proceeding to the Numerical Problems.

1. Methanol is used as a fuel in Indianapolis 500 race cars. Use the following table to determine whether methanol or 2,2,4-trimethylpentane (isooctane) releases more energy per liter during combustion.

Fuel	$\Delta H^\circ_{combustion}$(kJ/mol)	Density (g/mL)
methanol	−726.1	0.791
2,2,4-trimethylpentane	−5461.4	0.692

2. a. Use the enthalpies of combustion given in the following table to determine which organic compound releases the greatest amount of energy per gram during combustion.

Fuel	$\Delta H^\circ_{combustion}$(kJ/mol)
methanol	−726.1
1-ethyl-2-methylbenzene	−5210.2
n-octane	−5470.5

   b. Calculate the standard enthalpy of formation of 1-ethyl-2-methylbenzene.

3. Given the enthalpies of combustion, which organic compound is the best fuel per gram?

Fuel	ΔH°_f(kJ/mol)
ethanol	−1366.8
benzene	−3267.6
cyclooctane	−5434.7

Numerical Answers

1.

2.

a. To one decimal place

methanol: ΔH/g = −22.6 kJ

C_9H_{12}: ΔH/g = −43.3 kJ

octane: ΔH/g = −47.9 kJ

Octane provides the largest amount of heat per gram upon combustion.

b, $\Delta H_f(C_9H_{17})$ = −46.1 kJ/mol

5.7: Enthalpies of Formation

Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Conceptual Problems.

1. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.
2. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?
3. What is the difference between ΔH°_{f} and ΔH_{f}?
4. How can ΔH°_{f} of a compound be determined if the compound cannot be prepared by the reactions used to define its standard enthalpy of formation?
5. For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.
   a. HBr
   b. CH_3OH
   c. $NaHCO_3$
6. Describe the distinction between ΔH_{soln} and ΔH_{f}.
7. The following table lists ΔH°_{soln} values for some ionic compounds. If 1 mol of each solute is dissolved in 500 mL of water, rank the resulting solutions from warmest to coldest.

Compound	ΔH°_{soln}(kJ/mol)
KOH	–57.61
$LiNO_3$	–2.51
$KMnO_4$	43.56
$NaC_2H_3O_2$	–17.32

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Numerical Problems.

1. Using "Appendix A, calculate ΔH°_{rxn} for each chemical reaction.

   a. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

   b. $CaCO_3(s, \text{calcite}) \rightarrow CaO(s) + CO_2(g)$

   c. $AgNO_3(s) + NaCl(s) \rightarrow AgCl(s) + NaNO_3(s)$

2. Using "Appendix A, determine ΔH°_{rxn} for each chemical reaction.

   a. $2Na(s) + Pb(NO_3)_2(s) \rightarrow 2NaNO_3(s) + Pb(s)$

   b. $Na_2CO_3(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + CO_2(g) + H_2O(l)$

   c. $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

3. Calculate ΔH°_{rxn} for each chemical equation. If necessary, balance the chemical equations.

   a. $Fe(s) + CuCl_2(s) \rightarrow FeCl_2(s) + Cu(s)$

b. $(NH_4)_2SO_4(s) + Ca(OH)_2(s) \rightarrow CaSO_4(s) + NH_3(g) + H_2O(l)$

c. $Pb(s) + PbO_2(s) + H_2SO_4(l) \rightarrow PbSO_4(s) + H_2O(l)$

4. Calculate ΔH^o_{rxn} for each reaction. If necessary, balance the chemical equations.

   a. $4HBr(g) + O_2(g) \rightarrow 2H_2O(l) + 2Br_2(l)$

   b. $2KBr(s) + H_2SO_4(l) \rightarrow K_2SO_4(s) + 2HBr(g)$

   c. $4Zn(s) + 9HNO_3(l) \rightarrow 4Zn(NO_3)_2(s) + NH_3(g) + 3H_2O(l)$

5. Use the data in "Appendix A to calculate ΔH^o_f for the reaction $Sn(s, white) + 4HNO_3(l) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$.

6. Use the data in "Appendix A to calculate ΔH^o_f for the reaction $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(l)$.

7. How much heat is released or required in the reaction of 0.50 mol of HBr(g) with 1.0 mol of chlorine gas to produce bromine gas?

8. How much energy is released or consumed if 10.0 g of N_2O_5 is completely decomposed to produce gaseous nitrogen dioxide and oxygen?

9. In the mid-1700s, a method was devised for preparing chlorine gas from the following reaction:

$$NaCl(s) + H_2SO_4(l) + MnO_2(s) \rightarrow Na_2SO_4(s) + MnCl_2(s) + H_2O(l) + Cl_2(g)$$

   Calculate ΔH^o_{rxn} for this reaction. Is the reaction exothermic or endothermic?

10. Would you expect heat to be evolved during each reaction?

    1. solid sodium oxide with gaseous sulfur dioxide to give solid sodium sulfite
    2. solid aluminum chloride reacting with water to give solid aluminum oxide and hydrogen chloride gas

11. How much heat is released in preparing an aqueous solution containing 6.3 g of calcium chloride, an aqueous solution containing 2.9 g of potassium carbonate, and then when the two solutions are mixed together to produce potassium chloride and calcium carbonate.

Numerical Answers

1. a. –1203 kJ/mol O_2

   b. 179.2 kJ

   c. –59.3 kJ

2.
3.
4.

5. –174.1 kJ/mol

6.

7. –20.3 kJ

8.

9. –34.3 kJ/mol Cl_2; exothermic

10.

11. ΔH = −2.86 kJ $CaCl_2$: −4.6 kJ; K_2CO_3, −0.65 kJ; mixing, −0.28 kJ

5.8: Foods and Fuels

Conceptual Problems

1. Can water be considered a food? Explain your answer.
2. Describe how you would determine the caloric content of a bag of popcorn using a calorimeter.
3. Why do some people initially feel cold after eating a meal and then begin to feel warm?
4. In humans, one of the biochemical products of the combustion/digestion of amino acids is urea. What effect does this have on the energy available from these reactions? Speculate why conversion to urea is preferable to the generation of N_2.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Numerical Problems.

1. Determine the amount of energy available from the biological oxidation of 1.50 g of leucine (an amino acid, ΔH_{comb} = −3581.7 kJ/mol).

2. Calculate the energy released (in kilojoules) from the metabolism of 1.5 oz of vodka that is 62% water and 38% ethanol by volume, assuming that the total volume is equal to the sum of the volume of the two components. The density of ethanol is 0.824 g/mL. What is this enthalpy change in nutritional Calories?

3. While exercising, a person lifts an 80 lb barbell 7 ft off the ground. Assuming that the transformation of chemical energy to mechanical energy is only 35% efficient, how many Calories would the person use to accomplish this task? From Figure 9.4.2, how many grams of glucose would be needed to provide the energy to accomplish this task?

4. A 30 g sample of potato chips is placed in a bomb calorimeter with a heat capacity of 1.80 kJ/°C, and the bomb calorimeter is immersed in 1.5 L of water. Calculate the energy contained in the food per gram if, after combustion of the chips, the temperature of the calorimeter increases to 58.6°C from an initial temperature of 22.1°C.

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5.S: Thermochemistry (Summary)

- **thermodynamics** – study of energy and its transformations
- **thermochemistry** – relationships between chemical reactions and energy changes

5.1: The Nature of Energy

- **Force**: symbolized by *F*, any kind of push or pull exerted on an object
- **Work**: symbolized by *w*, movement of an object against some force

$$w = F \times d$$

- where *w* is work, *F* is force, and *d* is distance that the object is being moved
- **Heat**: energy that is transferred from one object to another because of difference in temperature
- **Energy**: the capacity to do work or to transfer heat

Kinetic and Potential Energy

Kinetic energy: energy of motion

$E_k = ½ mv^2$ where E_k is the kinetic energy, *m* is the mass, and *v* is the velocity.

Potential energy: energy that an object possesses as a result of its composition or its position with respect to another object

Energy Units

- **Joule**: SI unit for energy, 1J = kgm^2/s^2
- **Calorie**: abbreviated *cal*, originally defined as the amount of energy required to raise the temperature of 1 g of water by 1°C. 1 cal = 4.184 J

Systems and Surroundings

- **System**: portion singled out for study
- **Surroundings**: everything beyond the system

Systems exchanges energy with surroundings in the form of heat and work, but not matter

Lowering the Energy of the System

Systems tend to attain as low an energy as possible. Systems with a high potential energy are less stable and more likely to undergo change than systems with a low potential energy.

5.2: The First Law of Thermodynamics

First law of thermodynamics: aka **The Law of Conservation of Energy**; a statement of our experience that energy is conserved in any process. We can express the first law in many ways. One of the more useful expressions is that the change in internal energy, ΔE, of a system in any process is equal to the heat, *q*, added to the system, plus the work, *w*, done *on* the system by its surroundings: $\Delta E = q + w$.

Internal Energy

The total energy of a system is the sum of all the kinetic and potential energies of its components parts.

Internal energy: total energy of the system (see above)

Because there are so many types of motion and interactions, we cannot determine the exact energy of any system. However, we can measure the changes *in internal energy that accompany chemical and physical processes.*

$?E = E_{final} - E_{initial}$

$E_{final} > E_{initial}$ = system has gained energy

$E_{final} < E_{initial}$ = system has lost energy

Initial state refers to reactants, final state to products.

Relating ΔE to Heat and Work

The internal energy of a system changes in magnitude as heat is added to or removed from the system, or as work is done on it or by it.

?E = q + w where ΔE is internal energy, q is heat, and w is work

Heat added to the system is assigned a positive sign. Likewise, work on the system is positive. On the other hand, both the heat lost by the system and the work done by the system on its surroundings are negative; they reduce the internal energy.

Ex. A system absorbs 50 J of heat and does 10 J of work on its surroundings, q = 50 J and w = 10 J. Thus, ΔE = 50 J + (10 J) = 40 J.

State Functions

The total energy of a system is proportional to the total quantity of matter in the system; energy is an extensive property.

State function: a property of a system that is determined by the state or condition of the system and not by how it got to that state; its value is fixed when temperature, pressure, composition, and physical form are specified. The internal energy of a system is a state function.

The value of a state function does not depend on the particular history of the sample, only on its present condition. Because E is a state function, ΔE depends only on the initial and final states of the system and not on how the change occurs.

However, the work done by a system in a given process is not a state function!!!

5.3: Enthalpy

Heat flows between system and surroundings until *both are at the same temperature*.

Endothermic process: a process in which a system absorbs heat from its surroundings

Exothermic process: a process in which a system releases heat to its surroundings

Enthalpy

Enthalpy: represented by *H*; deals with the amount of heat absorbed or released during a chemical reaction under constant pressure

The change in enthalpy, ΔH, equals the heat, q_p, added to or lost by the system when the process occurs under constant pressure:

$?H = q_p$

(The subscript P on q is a reminder that we are considering a special case where pressures is constant)

$\Delta H = H_{final} - H_{initial}$

$H_{final} > H_{initial}$ = positive ΔH; system has gained heat from surroundings (endothermic)

$H_{final} < H_{initial}$ = negative ΔH; system has lost heat to the surroundings (exothermic)

5.4: Enthalpy of Reaction

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

Thermochemical equations: balanced chemical equations that show the associated enthalpy change

1. Enthalpy is an *extensive* property (depends on amount of matter present). *This fact means that the magnitude of ΔH is directly proportional to the amount of reactant consumed in the process*
2. The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction. *When we reverse a reaction, the reactants become the products, and vice versa. Reversing the products and reactants leads to the same magnitude but a change in sign for ΔH.*
3. The enthalpy change for a reaction depends on the state of the reactants and products.

5.5: Calorimetry

Calorimetry: measurement of heat flow

Calorimeter: apparatus that measures heat flow

Heat Capacity and Specific Heat

Heat capacity: amount of energy required to raise the temperature of a given object by 1°C. The greater the capacity of a body, the more heat it requires to raise its temperature.

Molar heat capacity: when referring to pure substances; heat capacity of 1 mol of substance

Specific heat: heat capacity of 1 g of a substance (as opposed to a mole)

Specific heat= quantity of heat transferred / (grams of substance) X (temperature change)

= q / m X ΔT

q = (specific heat) X (grams of substance) X Δ*T*

ConstantPressure Calorimetry

Calorimeters are simple instruments to control pressure. Because the calorimeter prevents the gain or loss of heat from its surroundings, the heat released by the reaction, q_{rxn}, equals that gained by the solution, q_{soln}. Thus,

$q_{rxn} = q_{soln}$ = (specific heat) X (grams of solution) X Δ*T*

Bomb Calorimetry

Bomb calorimeter: device for measuring the heat evolved in the combustion of a substance under constant volume conditions. Most used for combustion reactions.

$q_{evolved} = C_{calorimeter}$ X Δ*T* , where $C_{calorimeter}$ is the heat capacity of the calorimeter

5.6: Hess's Law

Because enthalpy is a state function, the enthalpy change, Δ*H*, associated with any chemical process depends only on the *amount of matter that undergoes change*, and on the nature of the *initial state of the reactants* and the *final state of the products*.

$CH_{4\ (g)} + 2O_{2\ (g)}$? $CO_{2\ (g)} + 2H_2O_{\ (g)}$ ΔH = 802 kJ

(Add) $2H_2O_{(g)}$? $2H_2O_{(l)}$?H = 88 kJ

_____

$CH_{4\ (g)} + 2O_{2\ (g)} + 2H_2O_{(g)} \rightarrow CO_{2\ (g)} + 2H_2O_{(l)} + 2H_2O_{(g)}$

Net equation:

$CH_{4\ (g)} + 2O_{2\ (g)}$? $CO_{2\ (g)} + 2H_2O_{(l)}$

To obtain the net equation, the sum of the reactants of the two equations is placed on one side of the arrow, and the sum of the products on the other side. Because $2H_2O_{(g)}$ occurs on both sides of the equation, it can be cancelled.

Hess's law: states that *if a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for individual steps*. The overall enthalpy change for the process is independent of the number of steps or the particular nature of the path by which the reaction is carried out.

The first law of thermodynamics, in the form of Hess's law, teaches us that we can never expect to obtain more (or less) energy from a chemical reaction by changing the method of carrying out the reaction.

5.7: Enthalpies of Formation

- *Enthalpies of vaporization* (ΔH for converting liquids to gas)
- *Enthalpies of fusion* (ΔH for melting solids)
- *Enthalpies of combustion* (ΔH for combusting a substance in oxygen)

Enthalpy of formation: aka **Heat of formation**; enthalpy change that accompanies the formation of a substance from the most stable forms of its component elements. Labeled ΔH_f, where the subscript f indicates that the substance has been formed from its elements.

The magnitude of any enthalpy change depends on the conditions of temperature, pressure, and state (gas, liquid, solid) of the reactants and product.

Standard state: for a substance is the form most stable at the particular temperature of interest and at standard atmospheric pressure.

Standard enthalpy of formation: $\Delta H°_f$. change in enthalpy that accompanies the formation of 1 mol of that substance from its elements, with all substances in their standard states.

Using Enthalpies of Formation to Calculate Enthalpies of Reaction

$$\Delta H°_{rxn} = \sum n\Delta H°_f \text{ (products) } \sum m\Delta H°_f \text{ (reactants)}$$

∑ = the sum of

m and n = stoichiometric coefficients of the chemical reaction

$C_3H_{8\ (g)} + 5O_{2\ (g)} \rightarrow 3CO_{2\ (g)} + 4H_2O_{(l)}$

$\Delta H°_{rxn} = [3\Delta H°_f (CO_2) + 4\Delta H°_f (H_2O)] - [\Delta H°_f (C_3H_8) + 5\Delta H°_f (O_2)]$

$\Delta H°_{rxn} = [(3 \text{ mol } CO_2) (393.5 \text{ kJ/mol}) + (4 \text{ mol } H_2O) (285.5 \text{ kJ/mol})]$

= (2324 kJ) – (1103.85 kJ)

=2220 kJ

5.8: Foods and Fuels

Fuel value: energy released when 1g of a material is combusted

Foods

- Main sources of energy for the body are from carbohydrates and fat
- Breakdown of carbohydrates is rapid, so energy is quickly supplied to the body
- Fats are well suited for the body because (1) they are insoluble in water, which permits their storage in the human body. (2) they produce more energy per gram thatneither proteins or carbohydrates.

Fuels

- **Fossil fuels**: coal, petroleum, and natural gas
- **Natural gas**: consists of gaseous hydrocarbons, compounds of hydrogen and carbon
- **Petroleum**: liquid composed of hundreds of compounds
- **Coal**: solid; contains hydrocarbons of high molecular weight as well as compounds containing sulfur, oxygen, and nitrogen. Most abundant fossil fuel
- **Syngas**: synthetic gas abbreviation

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6: ELECTRONIC STRUCTURE OF ATOMS

In this chapter, we describe how electrons are arranged in atoms and how the spatial arrangements of electrons are related to their energies. We also explain how knowing the arrangement of electrons in an atom enables chemists to predict and explain the chemistry of an element. As you study the material presented in this chapter, you will discover how the shape of the periodic table reflects the electronic arrangements of elements. In this and subsequent chapters, we build on this information to explain why certain chemical changes occur and others do not. After reading this chapter, you will know enough about the theory of the electronic structure of atoms to explain what causes the characteristic colors of neon signs, how laser beams are created, and why gemstones and fireworks have such brilliant colors. In later chapters, we will develop the concepts introduced here to explain why the only compound formed by sodium and chlorine is NaCl, an ionic compound, whereas neon and argon do not form any stable compounds, and why carbon and hydrogen combine to form an almost endless array of covalent compounds, such as CH_4, C_2H_2, C_2H_4, and C_2H_6. You will discover that knowing how to use the periodic table is the single most important skill you can acquire to understand the incredible chemical diversity of the elements.

6.1: The Wave Nature of Light

6.2: Quantized Energy and Photons

6.3: Line Spectra and the Bohr Model

6.4: The Wave Behavior of Matter

6.5: Quantum Mechanics and Atomic Orbitals

6.6: 3D Representation of Orbitals

6.7: Many-Electron Atoms

6.8: Electron Configurations

6.9: Electron Configurations and the Periodic Table

6.E: Electronic Structure of Atoms (Exercises)

6.S: Electronic Structure of Atoms (Summary)

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6.1: The Wave Nature of Light

Learning Objectives

- To learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves are among the types of electromagnetic waves.

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.



Figure 6.1.1: A Wave in Water. When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

Properties of Waves

A wave is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure 6.1.1). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

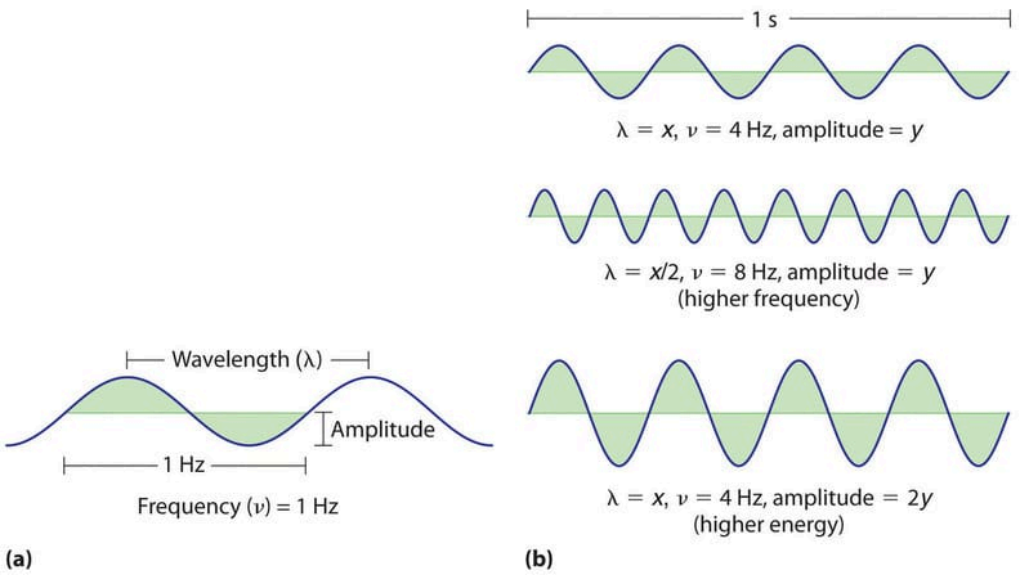


Figure 6.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 6.1.2). As you may have noticed in Figure 6.1.1, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the **wavelength** (λ, lowercase Greek lambda). Wavelengths are described by a unit of distance, typically meters. The **frequency** (u, lowercase Greek nu) of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations per second (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894), a pioneer in the field of electromagnetic radiation.

The **amplitude**, or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 6.1.2, two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

$$(\text{wavelength})(\text{frequency}) = \text{speed}$$

$$\lambda u = v \tag{6.1.1}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{\text{wave}}}{\text{second}}\right) = \frac{\text{meters}}{\text{second}} \tag{6.1.2}$$

> Be careful not to confuse the symbols for the speed, v, with the frequency, u.

Different types of waves may have vastly different possible speeds and frequencies. Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as **electromagnetic radiation**. (Figure 6.1.3). Some forms of electromagnetic radiation are shown in Figure 6.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which turns out to be a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (about 3.00 ×10^8 m/s or 1.86 × 10^5 mi/s). This is about a million times faster than the speed of sound.

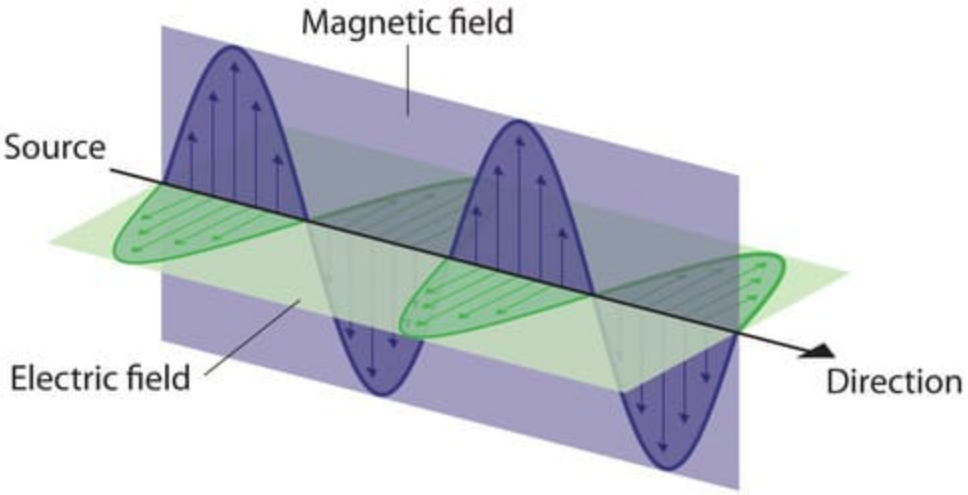


Figure 6.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (*c*), they differ in only wavelength and frequency. As shown in Figure 6.1.4 and Table 6.1.1, the wavelengths of familiar electromagnetic radiation range from 10^{1} m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing v with \(c\) in Equation 6.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda u \tag{6.1.3}$$

$$u = \frac{c}{\lambda} \tag{6.1.4}$$

For example, the frequency of radio waves is about 10^{8} Hz, whereas the frequency of gamma rays is about 10^{20} Hz. Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7×10^{-7} m (700 nm, or 4.3×10^{14} Hz) and 4×10^{-7} m (400 nm, or 7.5×10^{14} Hz). Note that when frequency increases, wavelength decreases; *c* being a constant stays the same. Similarly, when frequency decreases, the wavelength increases.

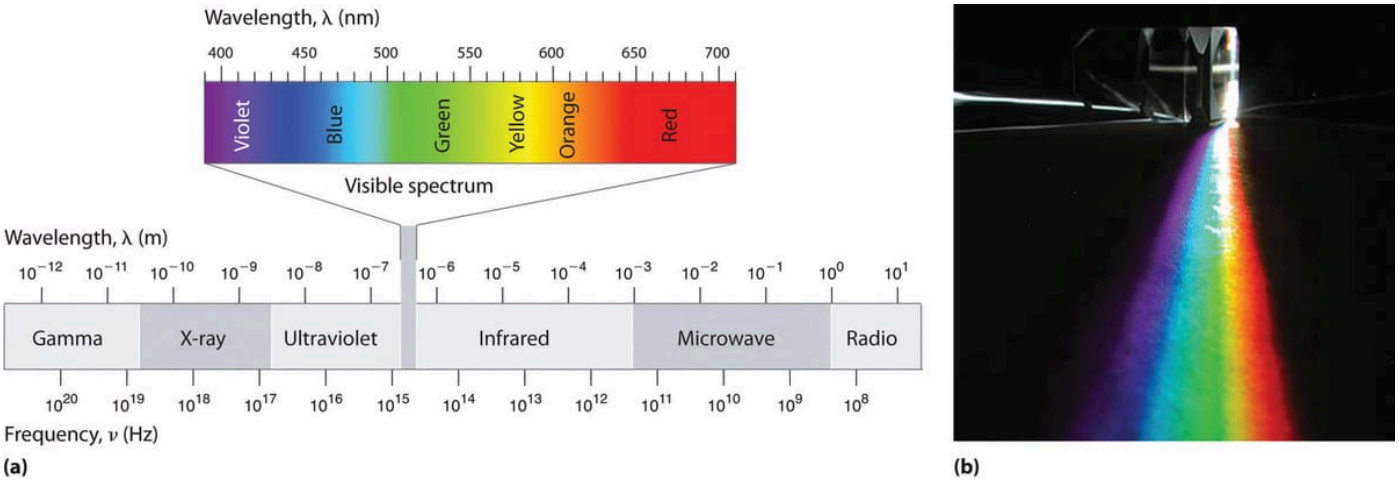


Figure 6.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Within the visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 6.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 6.1.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	UV, visible
micrometer	μm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto u \tag{6.1.5}$$

$$\propto \frac{1}{\lambda} \tag{6.1.6}$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer of the atmosphere absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

The energy of electromagnetic radiation increases with increasing frequency and decreasing wavelength.

YouTube Video

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Electromagnetic Radiation: https://youtu.be/TZy7a69pP-w

Example 6.1.1: Wavelength of Radiowaves

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 6.1.4 to calculate the wavelength in meters.

Solution:

From Equation 6.1.4, we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998 × 10^8 m/s:

$$\begin{aligned} \lambda\nu &= c \\ &= 2.998 \times 10^8 m/s \end{aligned}$$

Thus the wavelength λ is given by

$$\begin{aligned} \lambda &= \frac{c}{u} \\ &= \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \cancel{MHz}}\right)\left(\frac{1\ \cancel{MHz}}{10^6\ \cancel{s^{-1}}}\right) \\ &= 2.965\ m \end{aligned}$$

Exercise 6.1.1

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

Answer available at the end of this section.

Summary

Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A **wave** is a periodic oscillation by which energy is transmitted through space. All waves are **periodic**, repeating regularly in both space and time. Waves are characterized by several interrelated properties: **wavelength** (λ), the distance between successive waves; **frequency** (u), the number of waves that pass a fixed point per unit time; **speed** (v), the rate at which the wave propagates through space; and **amplitude**, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. **Electromagnetic radiation** consists of two perpendicular waves, one electric and one magnetic, propagating at the **speed of light** (c). Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ in their frequencies and wavelengths.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 6.1.1

8.45 mm

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6.2: Quantized Energy and Photons

Learning Objectives

- To understand how energy is quantized.

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could *not* be explained by the theories available at the time.

Blackbody Radiation

One phenomenon that seemed to contradict the theories of classical physics was blackbody radiation, which is electromagnetic radiation given off by a hot object. The wavelength (i.e. color) of radiant energy emitted by a blackbody depends on only its temperature, not its surface or composition. Hence an electric stove burner or the filament of a space heater glows dull red or orange when heated, whereas the much hotter tungsten wire in an incandescent light bulb gives off a yellowish light.



Figure 6.2.1: Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

The *intensity* of radiation is a measure of the energy emitted per unit area. A plot of the intensity of blackbody radiation as a function of wavelength for an object at various temperatures is shown in Figure 6.2.2. One of the major assumptions of classical physics was that energy increased or decreased in a smooth, continuous manner. For example, classical physics predicted that as wavelength decreased, the intensity of the radiation an object emits should increase in a smooth curve without limit at *all* temperatures, as shown by the broken line for 6000 K in Figure 6.2.2. Thus classical physics could not explain the sharp *decrease* in the intensity of radiation emitted at shorter wavelengths (primarily in the ultraviolet region of the spectrum), which was referred to as the "ultraviolet catastrophe." In 1900, however, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing (in what he called "an act of despair") that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 6.2.2, so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy,

a **quantum**.

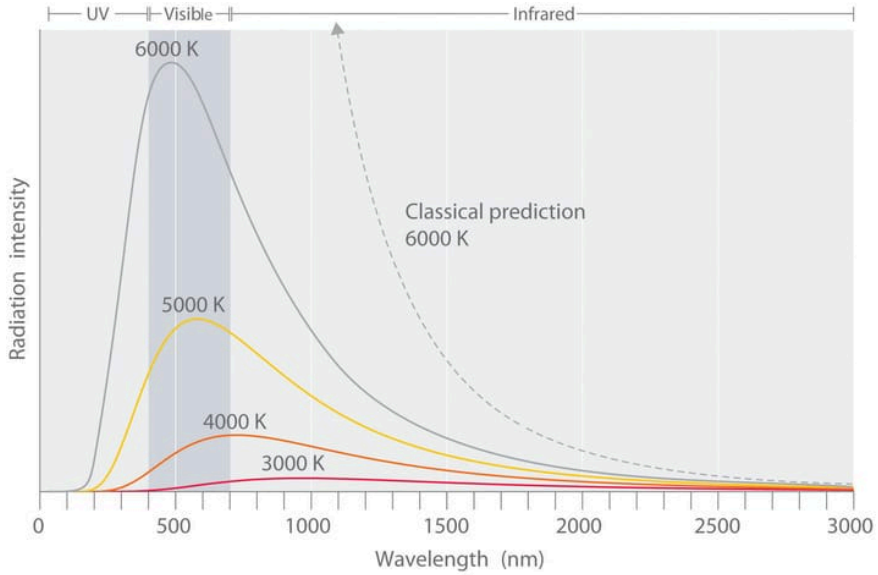
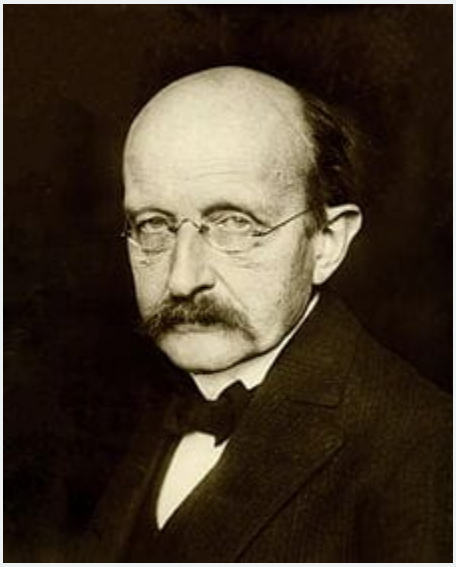


Figure 6.2.2: Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation it Emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure 6.2.1 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun (Figure 6.2.1). Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity.

Max Planck (1858–1947)

In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.



One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler, and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

Although quantization may seem to be an unfamiliar concept, we encounter it frequently. For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. Even electrical charge is quantized: an ion may have a charge of –1 or –2 but *not* –1.33 electron charges.

Planck postulated that the energy of a particular quantum of radiant energy could be described by the equation

$$E = hu \tag{6.2.1}$$

where the proportionality constant *h* is called Planck's constant, one of the most accurately known fundamental constants in science. For our purposes, its value to four significant figures is generally sufficient:

$$h = 6.626 \times 10^{-34}\, J \bullet s \,(\text{joule-segundos})$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of *h*ν, Planck devised an equation that fit the experimental data shown in Figure 6.2.2. We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 6.2.2, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

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Energy of a Photon: Energy of a Photon, YouTube(opens in new window) [youtu.be]

The Photoelectric Effect

Only five years after he proposed it, Planck's quantization hypothesis was used to explain a second phenomenon that conflicted with the accepted laws of classical physics. When certain metals are exposed to light, electrons are ejected from their surface (Figure 6.2.3). Classical physics predicted that the number of electrons emitted and their kinetic energy should depend on only the intensity of the light, not its frequency. In fact, however, each metal was found to have a characteristic threshold frequency of light; below that frequency, no electrons are emitted regardless of the light's intensity. Above the threshold frequency, the number of electrons emitted was found to be proportional to the intensity of the light, and their kinetic energy was proportional to the frequency. This phenomenon was called the photoelectric effect (A phenomenon in which electrons are ejected from the surface of a metal that has been exposed to light).

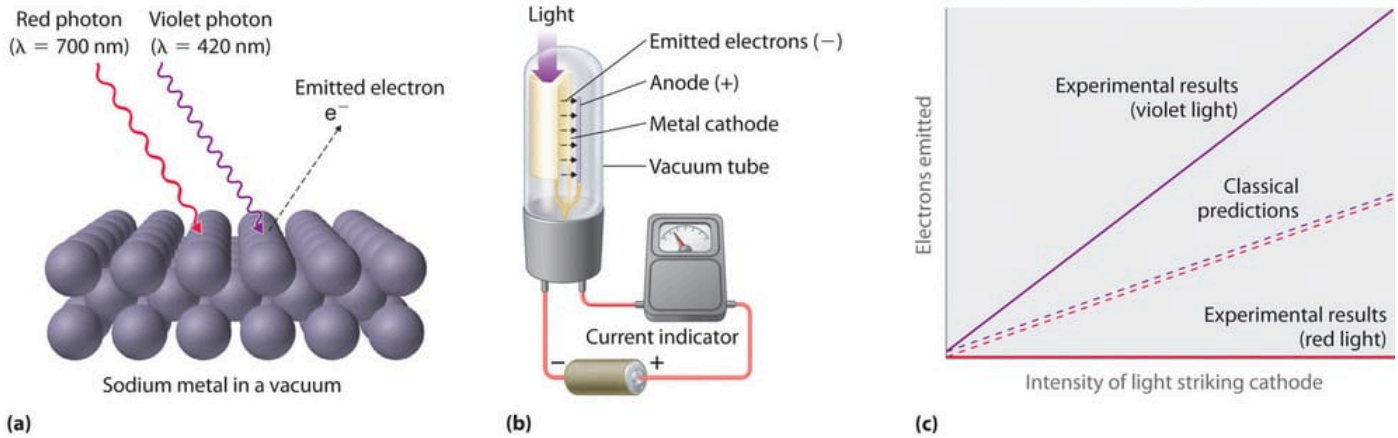


Figure 6.2.3: The Photoelectric Effect (a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons are emitted and attracted to the anode, resulting in a flow of electrical current. If the incoming light is interrupted by, for example, a passing person, the current drops to zero. (c) In contrast to predictions using classical physics, no electrons are emitted when photons of light with energy less than E_o, such as red light, strike the cathode. The energy of violet light is above the threshold frequency, so the number of emitted photons is proportional to the light's intensity.

Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) quickly realized that Planck's hypothesis about the quantization of radiant energy could also explain the photoelectric effect. The key feature of Einstein's hypothesis was the assumption that radiant energy arrives at the metal surface in particles that we now call **photons** (a quantum of radiant energy, each of which possesses a particular energy energy E given by Equation 6.2.1 Einstein postulated that each metal has a particular electrostatic attraction for its electrons that must be overcome before an electron can be emitted from its surface ($E_o = u_o$). If photons of light with energy less than E_o strike a metal surface, no single photon has enough energy to eject an electron, so no electrons are emitted regardless of the intensity of the light. If a photon with energy greater than E_o strikes the metal, then part of its energy is used to overcome the forces that hold the electron to the metal surface, and the excess energy appears as the kinetic energy of the ejected electron:

$$\begin{aligned} \text{kinetic energy of ejected electron} &= E - E_o \\ &= hu - hu_o \\ &= h\left(u - u_o\right) \end{aligned} \tag{6.2.2}$$

When a metal is struck by light with energy above the threshold energy E_o, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the *number* of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *frequency* of the light. Thus Einstein showed that the energy of the emitted electrons depended on the frequency of the light, contrary to the prediction of classical physics. Moreover, the idea that light could behave not only as a wave but as a particle in the form of photons suggested that matter and energy might not be such unrelated phenomena after all.

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The Photoelectric Effect: The Photoelectric Effect, YouTube(opens in new window) [youtu.be]

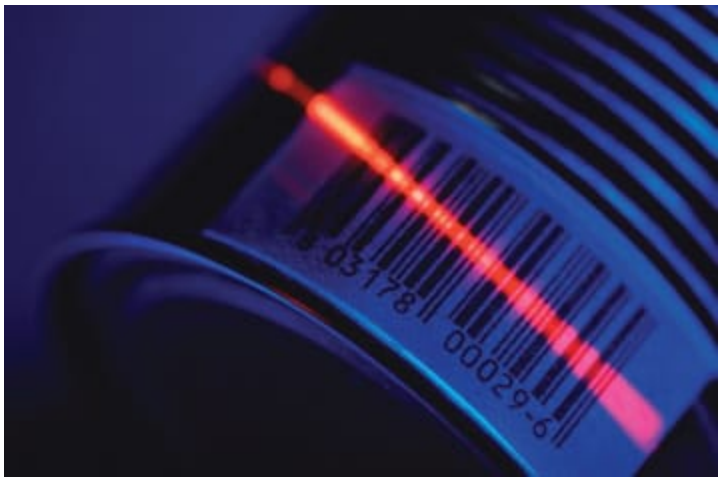
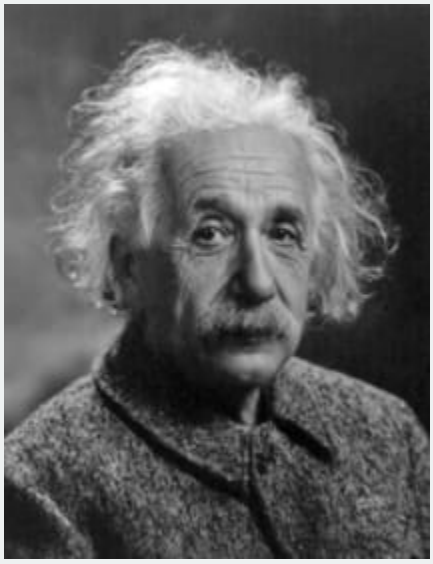


Figure 6.2.4: A Beam of Red Light Emitted by a Helium Neon laser reads a bar code. Originally Helium neon lasers, which emit red light at a wavelength of 632.8 nm, were used to read bar codes. Today, smaller, inexpensive diode lasers are used.

Albert Einstein (1879–1955)

In 1900, Einstein was working in the Swiss patent office in Bern. He was born in Germany and throughout his childhood his parents and teachers had worried that he might be developmentally disabled. The patent office job was a low-level civil service position that was not very demanding, but it did allow Einstein to spend a great deal of time reading and thinking about physics.



In 1905, his "miracle year" he published four papers that revolutionized physics. One was on the special theory of relativity, a second on the equivalence of mass and energy, a third on Brownian motion, and the fourth on the photoelectric effect, for which he received the Nobel Prize in 1921, the theory of relativity and energy-matter equivalence being still controversial at the time

Planck's and Einstein's postulate that energy is quantized is in many ways similar to Dalton's description of atoms. Both theories are based on the existence of simple building blocks, atoms in one case and quanta of energy in the other. The work of Planck

and Einstein thus suggested a connection between the quantized nature of energy and the properties of individual atoms.

Example 6.2.1

A ruby laser, a device that produces light in a narrow range of wavelengths emits red light at a wavelength of 694.3 nm (Figure 6.2.4). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

Use Equation 6.2.1 and the relationship between wavelength and frequency to calculate the energy in joules.

Solution:

The energy of a single photon is given by Equaton 6.2.1

$$E = hu = \frac{hc}{\lambda}.$$

Exercise 6.2.1

An x-ray generator, such as those used in hospitals, emits radiation with a wavelength of 1.544 Å.

a. What is the energy in joules of a single photon?
b. How many times more energetic is a single x-ray photon of this wavelength than a photon emitted by a ruby laser?

Answer a available at the end of this section.

External Videos and Examples

- Calculating Energy of a Mole of Photons_- Johnny Cantrell
- .Photons - ViaScience, an advanced explanation of the Planck radiation law and the photoelectric effect (below) as well as biological interactions with UV light.and the nature of light and quantum weirdness. Probably the first 6 minutes and the last 3 (from 12:00 on) as an introduction to wave particle duality.are useful to a beginning student.

- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Summary

The fundamental building blocks of energy are quanta and of matter are atoms. The properties of **blackbody radiation**, the radiation emitted by hot objects, could not be explained with classical physics. Max Planck postulated that energy was quantized and could be emitted or absorbed only in integral multiples of a small unit of energy, known as a **quantum**. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant h is a fundamental constant (Planck's constant). Albert Einstein used Planck's concept of the quantization of energy to explain the **photoelectric effect**, the ejection of electrons from certain metals when exposed to light. Einstein postulated the existence of what today we call **photons**, particles of light with a particular energy, $E = hu$. Both energy and matter have fundamental building blocks: quanta and atoms, respectively.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 6.2.1

$1.287 \times 10^{-15}\ J/photon$

4497 times

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6.3: Line Spectra and the Bohr Model

Learning Objectives

- To know the relationship between atomic spectra and the electronic structure of atoms.

The concept of the photon emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies.The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. However, more direct evidence was needed to verify the quantized nature of energy in all matter. In this section, we describe how observation of the interaction of atoms with visible light provided this evidence.

Line Spectra

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation, a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines of particular wavelengths, called a **line spectrum**, are observed rather than a continuous range of wavelengths (Figure $6.3.1$). The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.

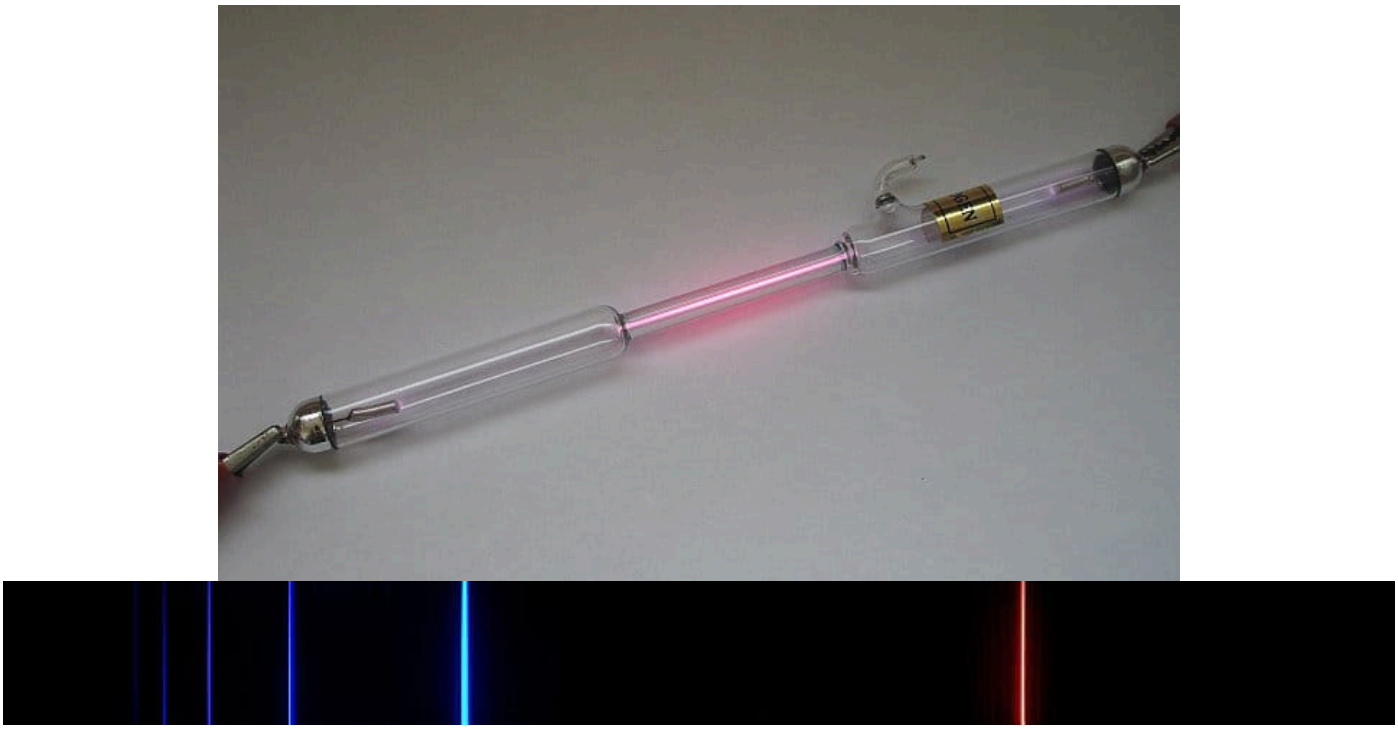


Figure $6.3.1$: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (CC BY-SA 3.0 Unported; Science Made Alive via Wikipedia) (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm. (CC BY-SA 3.0; Jan Homann via Wikipedia)

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge

because classical physics was unable to explain them. Part of the explanation is provided by Planck's equation: the observation of only a few values of λ (or u) in the line spectrum meant that only a few values of *E* were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

In 1885, a Swiss mathematics teacher, Johann Balmer (1825–1898), showed that the frequencies of the lines observed in the visible region of the spectrum of hydrogen fit a simple equation that can be expressed as follows:

$$u = constant\ \left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{6.3.1}$$

where *n* = 3, 4, 5, 6. As a result, these lines are known as the *Balmer series*. The Swedish physicist Johannes Rydberg (1854–1919) subsequently restated and expanded Balmer's result in the *Rydberg equation*:

$$\frac{1}{\lambda} = \Re\ \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{6.3.2}$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and $\Re$ the *Rydberg constant*, has a value of 1.09737 × 10^7 m^{-1}.

Johann Balmer (1825–1898)

A mathematics teacher at a secondary school for girls in Switzerland, Balmer was 60 years old when he wrote the paper on the spectral lines of hydrogen that made him famous.



Balmer published only one other paper on the topic, which appeared when he was 72 years old.

Like Balmer's equation, Rydberg's simple equation described the wavelengths of the visible lines in the emission spectrum of hydrogen (with n_1 = 2, n_2 = 3, 4, 5,...). More important, Rydberg's equation also predicted the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet (n_1 = 1, n_2 = 2, 3, 4,...) and one in the infrared (n_1 = 3, n_2 = 4, 5, 6). Unfortunately, scientists had not yet developed any theoretical justification for an equation of this form.

Bohr's Model

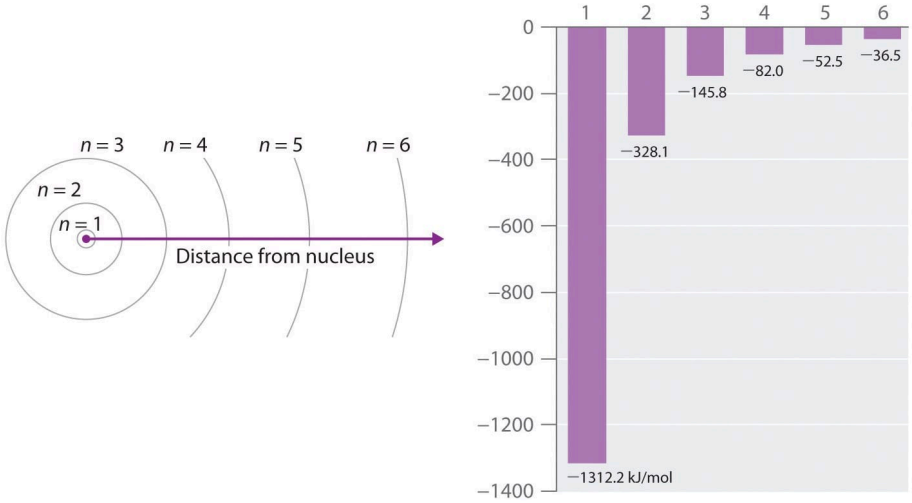
In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required only one assumption: *The electron moves around the nucleus*

in circular orbits that can have only certain allowed radii. Rutherford's earlier model of the atom had also assumed that electrons moved in circular orbits around the nucleus and that the atom was held together by the electrostatic attraction between the positively charged nucleus and the negatively charged electron. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space*.

Using classical physics, Niels Bohr showed that the energy of an electron in a particular orbit is given by

$$E_n = \frac{-\Re hc}{n^2} \tag{6.3.3}$$

where $\Re$ is the Rydberg constant, h is Planck's constant, c is the speed of light, and n is a positive integer corresponding to the number assigned to the orbit, with $n = 1$ corresponding to the orbit closest to the nucleus. In this model $n = \infty$ corresponds to the level where the energy holding the electron and the nucleus together is zero. In that level, the electron is unbound from the nucleus and the atom has been separated into a negatively charged (the electron) and a positively charged (the nucleus) ion. In this state the radius of the orbit is also infinite. The atom has been ionized.



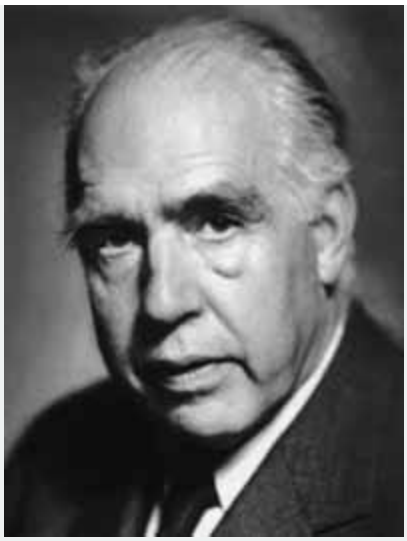
(a) Hydrogen orbits (Bohr model). Orbits are not drawn to scale.

(b) Hydrogen orbit energy (kJ/mol) vs. *n*

Figure 6.3.2: The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing *n*. (b) The energy of the orbit becomes increasingly less negative with increasing *n*.

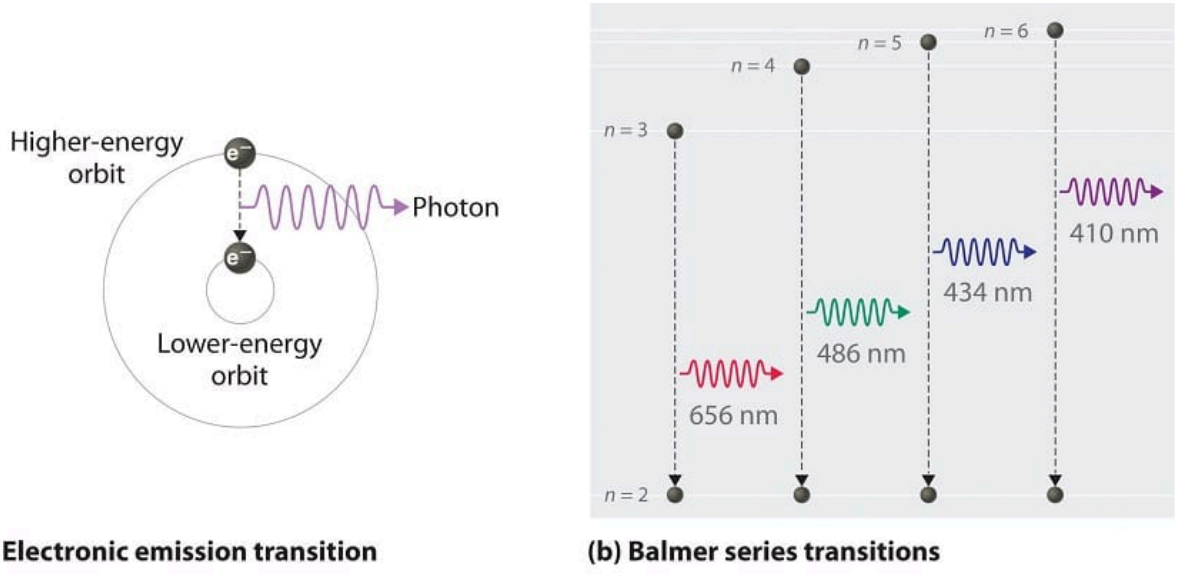
Niels Bohr (1885–1962)

During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project.



In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative, the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with n = 1 is the lowest lying and most tightly bound. The negative sign in Equation 6.3.3 indicates that the electron-nucleus pair is more tightly bound (i.e. at a lower potential energy) when they are near each other than when they are far apart. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the **ground state** (the most stable arrangement of electrons for an element or a compound) for a hydrogen atom. As n increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy (Figure 6.3.2*a*). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an **excited state**, defined as any arrangement of electrons that is higher in energy than the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called decay, it loses energy by emitting a photon whose energy corresponds to the *difference* in energy between the two states (Figure 6.3.1).



(a) Electronic emission transition **(b) Balmer series transitions**

Figure 6.3.3: The Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of *n* (at a higher energy) to an orbit with a lower value of *n* (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with *n* ≥ 3 to the orbit with *n* = 2. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.

So the difference in energy (ΔE) between any two orbits or energy levels is given by $\Delta E = E_{n_1} - E_{n_2}$ where n_1 is the final orbit

and n_2 the initial orbit. Substituting from Bohr's equation (Equation 6.3.3) for each energy value gives

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= -\frac{\Re hc}{n_2^2} - \left(-\frac{\Re hc}{n_1^2}\right) \\ &= -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)\end{aligned}$$

If $n_2 > n_1$, the transition is from a higher energy state (larger-radius orbit) to a lower energy state (smaller-radius orbit), as shown by the dashed arrow in part (a) in Figure 6.3.3. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{6.3.4}$$

Canceling hc on both sides gives

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{6.3.5}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equations 6.3.4 and 6.3.5 indicates that energy is released as the electron moves from orbit n_2 to orbit n_1 because orbit n_2 is at a higher energy than orbit n_1. Bohr calculated the value of $\Re$ from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of 1.0974 × 10^7 m^{-1}, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (6.3.3*b*); the lines in this series correspond to transitions from higher-energy orbits (n > 2) to the second orbit (n = 2). Thus the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state (n > 2) to a lower-energy state (n = 2) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the difference in energy between the two states (Figure 6.3.3*a*). The n = 3 to n = 2 transition gives rise to the line at 656 nm (red), the n = 4 to n = 2 transition to the line at 486 nm (green), the n = 5 to n = 2 transition to the line at 434 nm (blue), and the n = 6 to n = 2 transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the n = 3 than the n ≥ 4 levels. Consequently, the n = 3 to n = 2 transition is the most intense line, producing the characteristic red color of a hydrogen discharge (Figure 6.3.1*a*). Other families of lines are produced by transitions from excited states with n > 1 to the orbit with n = 1 or to orbits with n ≥ 3. These transitions are shown schematically in Figure 6.3.4

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The Bohr Atom: The Bohr Atom, YouTube(opens in new window) [youtu.be]

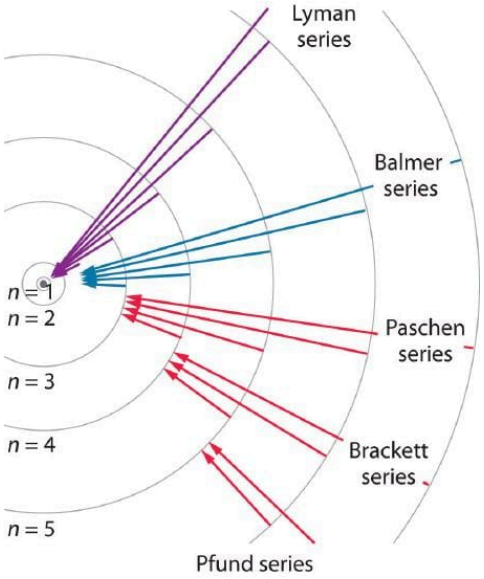


Figure 6.3.4: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)

Using Atoms to Time

In contemporary applications, electron transitions are used in timekeeping that needs to be exact. Telecommunications systems, such as cell phones, depend on timing signals that are accurate to within a millionth of a second per day, as are the devices that control the US power grid. Global positioning system (GPS) signals must be accurate to within a billionth of a second per day, which is equivalent to gaining or losing no more than one second in 1,400,000 years. Quantifying time requires finding an event with an interval that repeats on a regular basis.

To achieve the accuracy required for modern purposes, physicists have turned to the atom. The current standard used to calibrate clocks is the cesium atom. Supercooled cesium atoms are placed in a vacuum chamber and bombarded with microwaves whose frequencies are carefully controlled. When the frequency is exactly right, the atoms absorb enough energy to undergo an electronic transition to a higher-energy state. Decay to a lower-energy state emits radiation. The microwave frequency is continually adjusted, serving as the clock's pendulum.

In 1967, the second was defined as the duration of 9,192,631,770 oscillations of the resonant frequency of a cesium atom, called the *cesium clock*. Research is currently under way to develop the next generation of atomic clocks that promise to be even more accurate. Such devices would allow scientists to monitor vanishingly faint electromagnetic signals produced by nerve pathways in the brain and geologists to measure variations in gravitational fields, which cause fluctuations in time, that would aid in the discovery of oil or minerals.

Example 6.3.1: The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the n = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

A. Substitute the appropriate values into Equation 6.3.2 (the Rydberg equation) and solve for λ.
B. Use Figure 2.2.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

A For the Lyman series, n_1 = 1. The lowest-energy line is due to a transition from the n = 2 to n = 1 orbit because they are the closest in energy.

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1}$$

It turns out that spectroscopists (the people who study spectroscopy) use cm^{-1} rather than m^{-1} as a common unit. Wavelength is inversely proportional to energy but frequency is directly proportional as shown by Planck's formula, $E = hu$.

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly 200 - 5,000 cm^{-1}, the visible from 11,000 to 25.000 cm^{-1} and the UV between 25,000 and 100,000 cm^{-1}. The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1}.

$$\tilde{u} = \frac{1}{\lambda} = 8.228 \times 10^6\ \cancel{m^{-1}}\left(\frac{\cancel{m}}{100\ cm}\right) = 82,280\ cm^{-1}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets, producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone.

B This wavelength is in the ultraviolet region of the spectrum.

Exercise 6.3.1: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the n = 5 orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer available at the end of this section.

Bohr's model of the hydrogen atom gave an exact explanation for its observed emission spectrum. The following are his key contributions to our understanding of atomic structure:

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of tinkering, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element other than hydrogen (Figure 6.3.5). In fact, Bohr's model worked only for species that contained just one electron: H, He^+, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

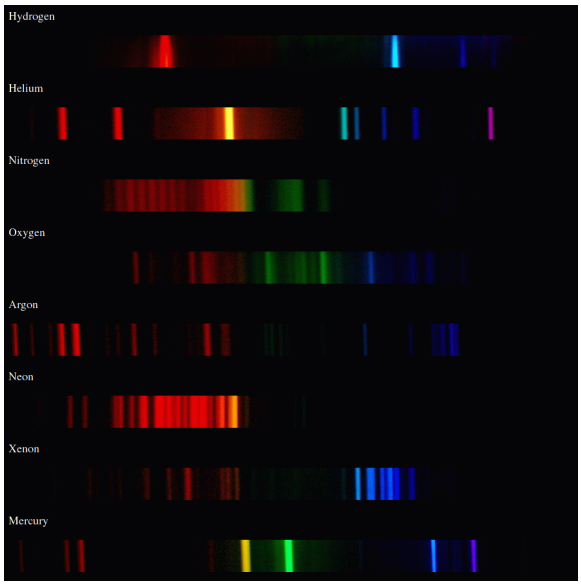


Figure 6.3.5: The atomic emission spectra for various elements. Each thin band in each spectrum corresponds to a single, unique transition between energy levels in an atom. Astronomical spectra image(opens in new window) from the Rochester Institute of Technology, CC BY-NC-SA 2.0(opens in new window).

The Energy States of the Hydrogen Atom

Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrum (a spectrum produced by the emission of light by atoms in excited states). The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrum (a spectrum produced by the absorption of light by ground-state atoms).

> When an atom emits light, it decays to a lower energy state; when an atom absorbs light, it is excited to a higher energy state.

If white light is passed through a sample of hydrogen, hydrogen atoms absorb energy as an electron is excited to higher energy levels (orbits with $n \geq 2$). If the light that emerges is passed through a prism, it forms a continuous spectrum with *black* lines (corresponding to no light passing through the sample) at 656, 468, 434, and 410 nm. These wavelengths correspond to the $n = 2$ to $n = 3$, $n = 2$ to $n = 4$, $n = 2$ to $n = 5$, and $n = 2$ to $n = 6$ transitions. Any given element therefore has both a characteristic emission spectrum and a characteristic absorption spectrum, which are essentially complementary images.

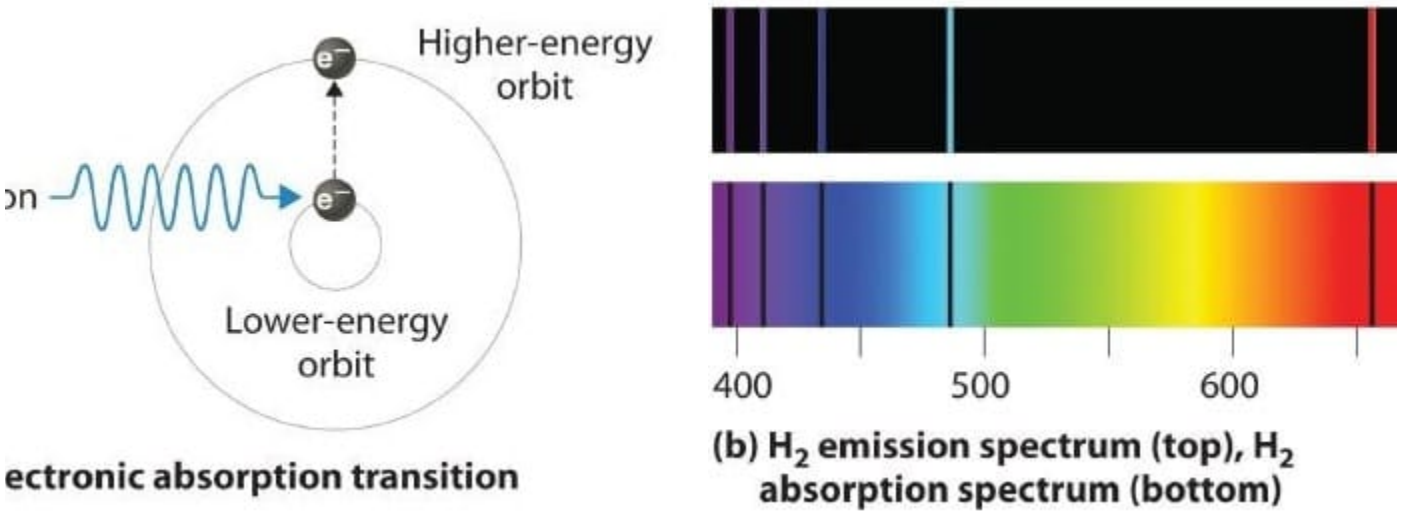


Figure 6.3.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here. (CC BY-NC-SA 3.0; anonymous)

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 6.3.7 Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning “sun.” Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium pick up electrons from the rocks to form helium atoms.

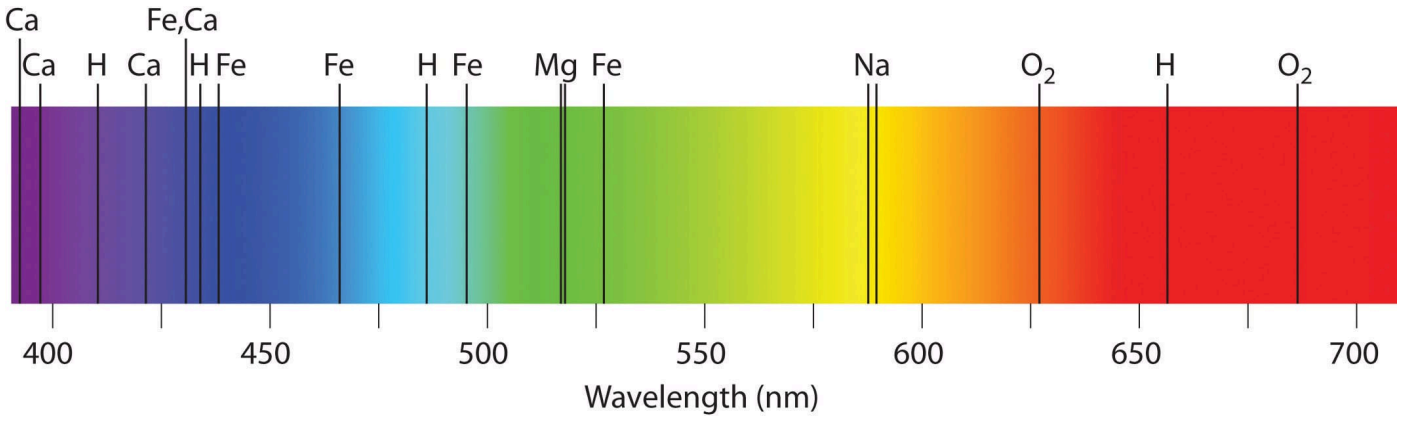


Figure 6.3.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun’s atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth’s atmosphere. (CC BY-NC-SA 3.0; anonymous)

The familiar red color of neon signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 6.3.5 . Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure 6.3.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

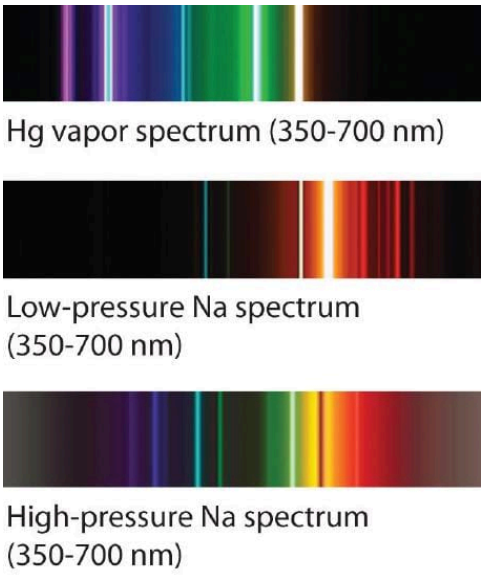


Figure 6.3.8: The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is cause by absorption of light in the cooler outer part of the lamp.

Summary

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element. Bohr's model revolutionized the understanding of the atom but could not explain the spectra of atoms heavier than hydrogen.

Key Concepts

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 6.3.1: The Pfund Series

4.65×10^3 nm; infrared

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6.4: The Wave Behavior of Matter

Learning Objectives

- To understand the wave–particle duality of matter.

Einstein's photons of light were individual packets of energy having many of the characteristics of particles. Recall that the collision of an electron (a particle) with a sufficiently energetic photon can eject a *photoelectron* from the surface of a metal. Any excess energy is transferred to the electron and is converted to the kinetic energy of the ejected electron. Einstein's hypothesis that energy is concentrated in localized bundles, however, was in sharp contrast to the classical notion that energy is spread out uniformly in a wave. We now describe Einstein's theory of the relationship between energy and mass, a theory that others built on to develop our current model of the atom.

The Wave Character of Matter

Einstein initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his special theory of relativity, which related energy and mass according to the famous equation:

$$E = hu = h\frac{c}{\lambda} = mc^2 \tag{6.4.1}$$

According to this theory, a photon of wavelength λ and frequency u has a nonzero mass, which is given as follows:

$$m = \frac{E}{c^2} = \frac{hu}{c^2} = \frac{h}{\lambda c} \tag{6.4.2}$$

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle duality (a principle that matter and energy have properties typical of both waves and particles). Depending on conditions, light could be viewed as either a wave or a particle.

In 1922, the American physicist Arthur Compton (1892–1962) reported the results of experiments involving the collision of x-rays and electrons that supported the particle nature of light. At about the same time, a young French physics student, Louis de Broglie (1892–1972), began to wonder whether the converse was true: Could particles exhibit the properties of waves? In his PhD dissertation submitted to the Sorbonne in 1924, de Broglie proposed that a particle such as an electron could be described by a wave whose wavelength is given by

$$\lambda = \frac{h}{mv} \tag{6.4.3}$$

where

- h is Planck's constant,
- m is the mass of the particle, and
- v is the velocity of the particle.

This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie's equation, which is an extremely small number. As you will calculate in Example 6.4.1, Planck's constant (6.63×10^{-34} J•s) is so small that the wavelength of a particle with a large mass is too short (less than the diameter of an atomic nucleus) to be noticeable.

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The de Broglie Equation: The de Broglie Equation, YouTube(opens in new window) [youtu.be]

Example 6.4.1: Wavelength of a Baseball in Motion

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

Given: mass and speed of object

Asked for: wavelength

Strategy:

A. Convert the speed of the baseball to the appropriate SI units: meters per second.
B. Substitute values into Equation 6.4.3 and solve for the wavelength.

Solution:

The wavelength of a particle is given by $\lambda = h/mv$. We know that m = 0.149 kg, so all we need to find is the speed of the baseball:

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right)$$

B Recall that the joule is a derived unit, whose units are (kg•m^2)/s^2. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} = \frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}^{\cancel{-2}} \cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m} \cdot \cancel{s^{-1}}\right)} = 9.95 \times 10^{-35}\ m$$

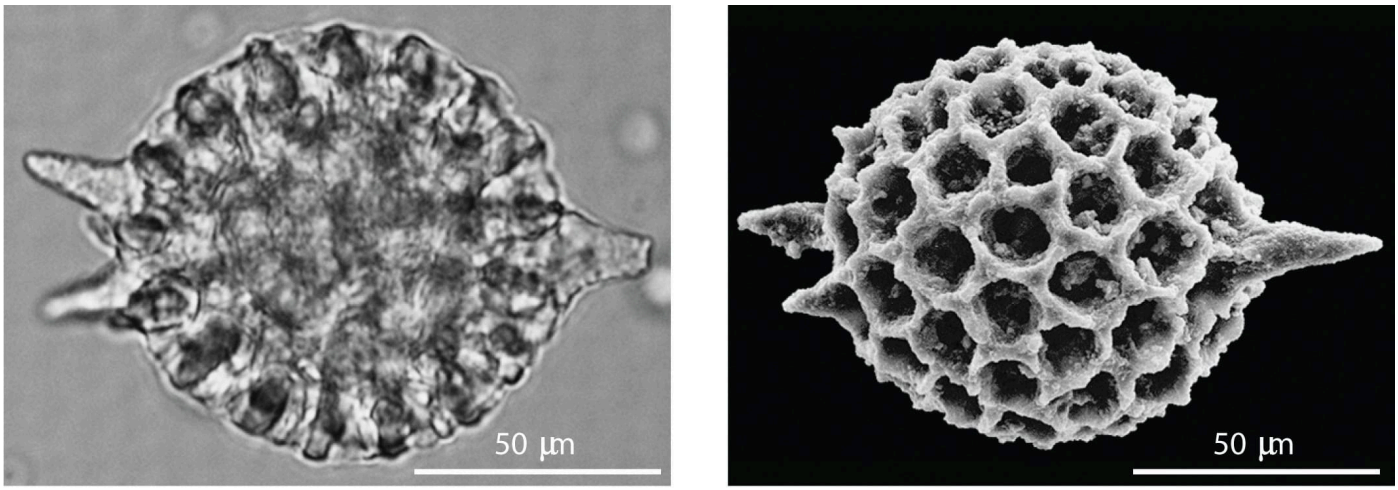
(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

Exercise 6.4.1: Wavelength of a Neutron in Motion

Calculate the wavelength of a neutron that is moving at 3.00 × 10^3 m/s.

Answer available at the end of this section.

As you calculated in Example 6.4.1, objects such as a baseball or a neutron have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, however, such as electrons, exhibit the properties of both particles *and* waves. Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can (Figure 6.4.1).



(a) Radiolarian under light microscope **(b) Radiolarian under electron microscope**

Figure 6.4.1: A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope. Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). (Radiolaria, which are shown here, are unicellular planktonic organisms.)

An Important Wave Property: Phase And Interference

A wave is a disturbance that travels in space. The magnitude of the wave at any point in space and time varies sinusoidally. While the absolute value of the magnitude of one wave at any point is not very important, the *relative* displacement of two waves, called the phase difference, is vitally important because it determines whether the waves reinforce or interfere with each other. Figure 6.4.2A shows an arbitrary phase difference between two wave and Figure 6.4.2B shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 6.4.2C shows what happens when the two lines are in phase, exactly superimposed on each other. Again, the green line is the sum of the intensities. A pattern of constructive and destructive interference is obtained when two (or more) diffracting waves interact with each other. This principle of diffraction and interference was used to prove the wave properties of electrons and is the basis for how electron microscopes work.

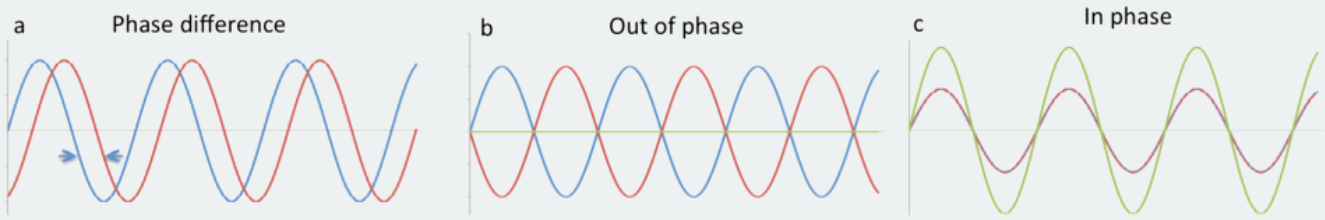
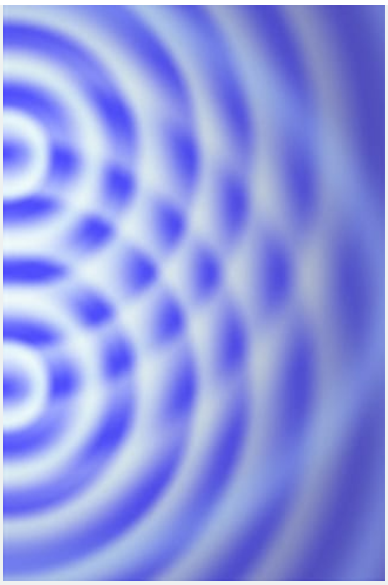


Figure 6.4.2: Phase. Two waves traveling together are displaced by a phase difference. If the phase difference is 0° then they lay on top of each other and reinforce. If the phase difference is 180° they completely cancel each other out.

A shows two waves with a phase difference where the peaks are slightly misaligned. B shows two waves out of phase, the two waves are opposite of each other. C shows two waves in phase, the two waves peak at the same time.



The waves are the white circles that start from the left side. The waves intersect at multiple points.

Photograph of an interference pattern produced by circular water waves in a ripple tank.

For a mathematical analysis of phase aspects in sinusoids, check the math Libretexts library.

Standing Waves

De Broglie also investigated why only certain orbits were allowed in Bohr's model of the hydrogen atom. He hypothesized that the electron behaves like a **standing wave** (a wave that does not travel in space). An example of a standing wave is the motion of a string of a violin or guitar. When the string is plucked, it vibrates at certain fixed frequencies because it is fastened at both ends (Figure $6.4.3$). If the length of the string is L, then the lowest-energy vibration (the fundamental) has wavelength

$$\frac{\lambda}{2} = L$$
$$\lambda = 2L$$

Higher-energy vibrations are called *overtones* (the vibration of a standing wave that is higher in energy than the fundamental vibration) and are produced when the string is plucked more strongly; they have wavelengths given by

$$\lambda = \frac{2L}{n} \tag{6.4.4}$$

where n has any integral value. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. Thus, we can think of the resonant frequencies of the string as being quantized. Notice in Figure $6.4.3$ that all overtones have one or more nodes, points where the string does not move. The amplitude of the wave at a node is zero.

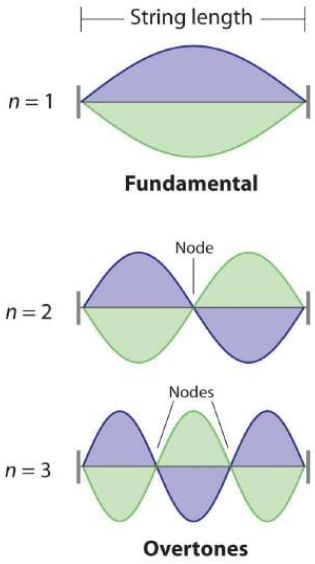


Figure 6.4.3: Standing Waves on a Vibrating String. The vibration with \(*n* = 1\) is the fundamental and contains no nodes. Vibrations with higher values of *n* are called overtones; they contain \(*n* − 1\) nodes.

Quantized vibrations and overtones containing nodes are not restricted to one-dimensional systems, such as strings. A two-dimensional surface, such as a drumhead, also has quantized vibrations. Similarly, when the ends of a string are joined to form a circle, the only allowed vibrations are those with wavelength

$$2\pi r = n\lambda \tag{6.4.5}$$

where r is the radius of the circle. De Broglie argued that Bohr's allowed orbits could be understood if the electron behaved like a *standing circular wave* (Figure 6.4.4). The standing wave could exist only if the circumference of the circle was an integral multiple of the wavelength such that the propagated waves were all in phase, thereby increasing the net amplitudes and causing *constructive interference*. Otherwise, the propagated waves would be out of phase, resulting in a net decrease in amplitude and causing *destructive interference*. The nonresonant waves interfere with themselves! De Broglie's idea explained Bohr's allowed orbits and energy levels nicely: in the lowest energy level, corresponding to $n = 1$ in Equation 6.4.5, one complete wavelength would close the circle. Higher energy levels would have successively higher values of *n* with a corresponding number of nodes.

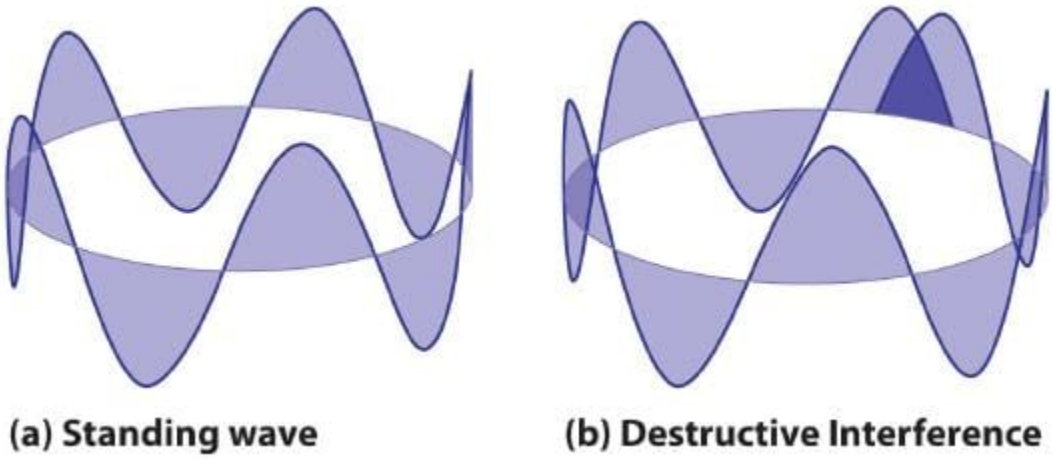


Figure 6.4.4: Standing Circular Wave and Destructive Interference. (a) In a standing circular wave with \(*n* = 5\), the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of the circle is not equal to an integral multiple of wavelengths, then the wave does not overlap exactly with itself, and the resulting destructive interference will result in cancellation of the wave. Consequently, a standing wave cannot exist under these conditions.

Like all analogies, although the standing wave model helps us understand much about why Bohr's theory worked, it also, if pushed too far, can mislead. As you will see, some of de Broglie's ideas are retained in the modern theory of the electronic structure of

the atom: the wave behavior of the electron and the presence of nodes that increase in number as the energy level increases. Unfortunately, his (and Bohr's) explanation also contains one major feature that we now know to be incorrect: in the currently accepted model, the electron in a given orbit is *not* always at the same distance from the nucleus.

The Heisenberg Uncertainty Principle

Because a wave is a disturbance that travels in space, it has no fixed position. One might therefore expect that it would also be hard to specify the exact position of a *particle* that exhibits wavelike behavior. A characteristic of light is that is can be bent or spread out by passing through a narrow slit. You can literally see this by half closing your eyes and looking through your eye lashes. This reduces the brightness of what you are seeing and somewhat fuzzes out the image, but the light bends around your lashes to provide a complete image rather than a bunch of bars across the image. This is called diffraction.

This behavior of waves is captured in Maxwell's equations (1870 or so) for electromagnetic waves and was and is well understood. An "uncertainty principle" for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. De Broglie's idea of wave-particle duality means that particles such as electrons which exhibit wavelike characteristics will also undergo diffraction from slits whose size is on the order of the electron wavelength.

This situation was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that “at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty relation.” Mathematically, the **Heisenberg uncertainty principle** states that the uncertainty in the position of a particle (Δx) multiplied by the uncertainty in its momentum [$\Delta(mv)$] is greater than or equal to Planck’s constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geq \frac{h}{4\pi} \tag{6.4.6}$$

Because Planck’s constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie’s equation to have measurable wavelengths.

If the precise position x of a particle is known absolutely ($\Delta x = 0$), then the uncertainty in its momentum must be infinite:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{6.4.7}$$

Because the mass of the electron at rest (m) is both constant and accurately known, the uncertainty in $\Delta(mv)$ must be due to the Δv term, which would have to be infinitely large for $\Delta(mv)$ to equal infinity. That is, according to Equation 6.4.7, the more accurately we know the exact position of the electron (as $\Delta x \to 0$), the less accurately we know the speed and the kinetic energy of the electron (1/2 mv^2) because $\Delta(mv) \to \infty$. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as $\Delta(mv) \to 0$], then $\Delta x \to \infty$ and we have no idea where the electron is.

Bohr’s model of the hydrogen atom violated the Heisenberg uncertainty principle by trying to specify *simultaneously* both the position (an orbit of a particular radius) and the energy (a quantity related to the momentum) of the electron. Moreover, given its mass and wavelike nature, the electron in the hydrogen atom could not possibly orbit the nucleus in a well-defined circular path as predicted by Bohr. You will see, however, that the *most probable radius* of the electron in the hydrogen atom is exactly the one predicted by Bohr’s model.

Example 6.4.1: Quantum Nature of Baseballs

Calculate the minimum uncertainty in the position of the pitched baseball from Example 6.4.1 that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

Given: mass and speed of object

Asked for: minimum uncertainty in its position

Strategy:

A. Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 6.4.6) to solve for the minimum uncertainty in the position of an object (Δx).
B. Find Δv by converting the velocity of the baseball to the appropriate SI units: meters per second.
C. Substitute the appropriate values into the expression for the inequality and solve for Δx.

Solution:

A The Heisenberg uncertainty principle (Equation 6.4.6) tells us that

$$(\Delta x)(\Delta(mv)) = h/4\pi$$

. Rearranging the inequality gives

$$\Delta x \geq \left(\frac{h}{4\pi}\right)\left(\frac{1}{\Delta(mv)}\right)$$

B We know that h = 6.626 × 10^{-34} J•s and m = 0.149 kg. Because there is no uncertainty in the mass of the baseball, $\Delta(mv) = m\Delta v$ and Δv = ±1 mi/h. We have

$$\Delta u = \left(\frac{1\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 0.4469\ m/s$$

C Therefore,

$$\Delta x \geq \left(\frac{6.626 \times 10^{-34}\ J \cdot s}{4\,(3.1416)}\right)\left(\frac{1}{(0.149\ kg)\,(0.4469\ m \cdot s^{-1})}\right)$$

Inserting the definition of a joule (1 J = 1 kg•m^2/s^2) gives

$$\Delta x \geq \left(\frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot s}{4\,(3.1416)\left(\cancel{s^2}\right)}\right)\left(\frac{1\ \cancel{s}}{\left(0.149\ \cancel{kg}\right)(0.4469\ \cancel{m})}\right)$$

$$\Delta x \geq 7.92 \pm \times 10^{-34}\ m$$

This is equal to 3.12×10^{-32} inches. We can safely say that if a batter misjudges the speed of a fastball by 1 mi/h (about 1%), he will not be able to blame Heisenberg's uncertainty principle for striking out.

Exercise 6.4.2

Calculate the minimum uncertainty in the position of an electron traveling at one-third the speed of light, if the uncertainty in its speed is ±0.1%. Assume its mass to be equal to its mass at rest.

Answer available at the end of this section.

Videos and Examples

- de Broglie Waves - Sixty Symbols - a bit of history and explanation (as well as wave particle duality can be explained)
- Calculating the wavelength of a proton - Josh Samson
- Calculating the wavelength of a small car - Prof. Heath
- What is the Uncertainty Principle? - Minute Physics
- AP Chem Heisenberg Uncertainty Principle - Mind Bite
- deBroglie Example - about education
- Heisenberg uncertainty principle quiz worked out - C Craig
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek

Answers for these quizzes are included.

Summary

An electron possesses both particle and wave properties. The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called **wave–particle duality**. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle.

$$\lambda = \frac{h}{mv}$$

The electron in Bohr's circular orbits could thus be described as a **standing wave**, one that does not move through space. Standing waves are familiar from music: the lowest-energy standing wave is the **fundamental** vibration, and higher-energy vibrations are **overtones** and have successively more **nodes**, points where the amplitude of the wave is always zero. Werner Heisenberg's **uncertainty principle** states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi}$$

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 6.4.1**: Wavelength of a Neutron in Motion**

1.32 Å, or 132 pm

Exercise 6.4.2

6×10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

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6.5: Quantum Mechanics and Atomic Orbitals

Learning Objectives

- To apply the results of quantum mechanics to chemistry.

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies.

Erwin Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wavefunctions* that are the solutions of Schrödinger's equations.

Wavefunctions

A wavefunction (Ψ) is a mathematical function that relates the location of an electron at a given point in space (identified by x, y, and z coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wavefunction is associated with a particular energy E. The properties of wavefunctions derived from quantum mechanics are summarized here:

- **A wavefunction uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates x, y, and z), and one specifies the time at which the object is at the specified location. For example, if you were the captain of a ship trying to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure $6.5.1$). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

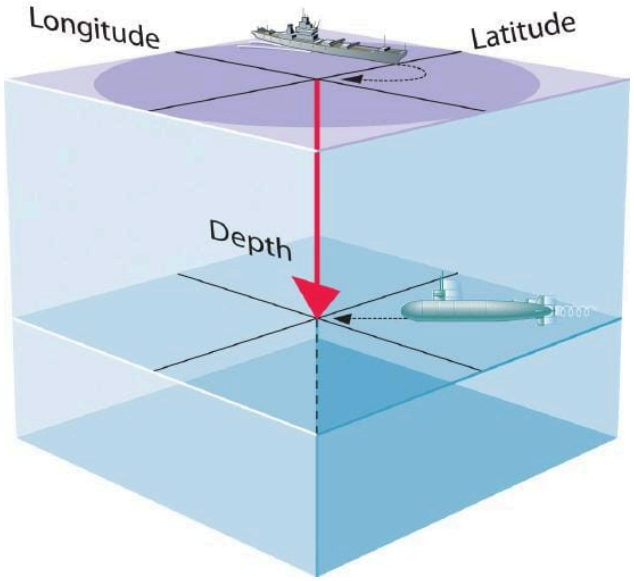


Figure 6.5.1: The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object

- **The magnitude of the wavefunction at a particular point in space is proportional to the amplitude of the wave at that point.** Many wavefunctions are complex functions, which is a mathematical term indicating that they contain $\sqrt{-1}$, represented as i. Hence the amplitude of the wave has no real physical significance. In contrast, the sign of the wavefunction (either positive or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding. The sign of the wavefunction should *not* be confused with a positive or negative electrical charge.
- **The square of the wavefunction at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The square of the wavefunction (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] and is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wavefunction Ψ and its complex conjugate Ψ*, in which all terms that contain *i* are replaced by $-i$. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 6.5.2.
- **Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wavefunction.** From the patterns of one- and two-dimensional standing waves shown previously, you might expect (correctly) that the patterns of three-dimensional standing waves would be complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a flooded planet. Schrödinger incorporated Legendre's equations into his wavefunctions. The requirement that the waves must be in phase with one another to avoid cancellation and produce a standing wave results in a limited number of solutions (wavefunctions), each of which is specified by a set of numbers called quantum numbers.
- **Each wavefunction is associated with a particular energy.** As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.

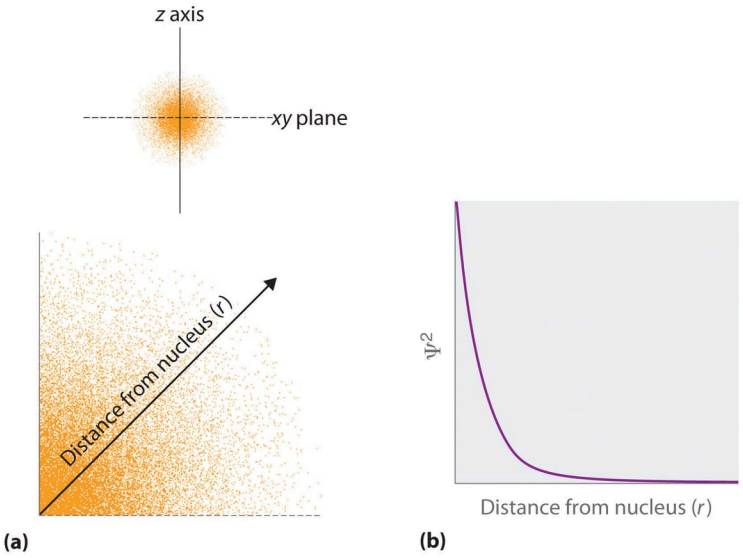


Figure 6.5.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus *r* for the ground state of the hydrogen atom, the electron probability density is greatest at *r* = 0 (the nucleus) and falls off with increasing *r*. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of *r* is very small but *not* zero.

Quantum Numbers

Schrödinger's approach uses three quantum numbers (*n*, *l*, and m_l) to specify any wavefunction. The quantum numbers provide information about the spatial distribution of an electron. Although *n* can be any positive integer, only certain values of *l* and m_l are allowed for a given value of *n*.

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \ldots \tag{6.5.1}$$

As *n* increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of *n* are easier to remove from an atom. All wavefunctions that have the same value of *n* are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number *n* corresponds to the *n* used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the **azimuthal quantum number (l)**. The value of *l* describes the *shape* of the region of space occupied by the electron. The allowed values of *l* depend on the value of *n* and can range from 0 to *n* − 1:

$$l = 0, 1, 2, \ldots, n - 1 \tag{6.5.2}$$

For example, if *n* = 1, *l* can be only 0; if *n* = 2, *l* can be 0 or 1; and so forth. For a given atom, all wavefunctions that have the same values of both *n* and *l* form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

YouTube Video

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Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell:
Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell, YouTube(opens in new window) [youtu.be]

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of *l*: m_l can range from –*l* to *l* in integral steps:

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{6.5.3}$$

For example, if $l = 0$, m_l can be only 0; if *l* = 1, m_l can be –1, 0, or +1; and if *l* = 2, m_l can be –2, –1, 0, +1, or +2.

Each wavefunction with an allowed combination of *n*, *l*, and m_l values describes an atomic **orbital**, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Example6.5.1: n=4 Shell Structure

How many subshells and orbitals are contained within the principal shell with *n* = 4?

Given: value of *n*

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given *n* = 4, calculate the allowed values of *l*. From these allowed values, count the number of subshells.
B. For each allowed value of *l*, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that *l* can have all integral values from 0 to *n* – 1. If *n* = 4, then *l* can equal 0, 1, 2, or 3. Because the shell has four values of *l*, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l.

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to $n^2 = 16$

Exercise 6.5.1: n=3 Shell Structure

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer available at the end of this section.

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital

l =	0	1	2	3
Designation	s	*p*	*d*	*f*

The principal quantum number is named first, followed by the letter s, *p*, *d*, or *f* as appropriate. (These orbital designations are derived from historical terms for corresponding spectroscopic characteristics: sharp, *p*rinciple, *d*iffuse, and *f*undamental.) A 1s orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = -1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = -2$, −1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 6.5.1):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible (1s); for $n = 2$, there are two subshells (2*s* and 2*p*); for $n = 3$, there are three subshells (3s, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with $n \geq 2$ also has an *np* subshell, and any shell with $n \geq 3$ also has an *nd* subshell. Because a 2*d* subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2*d* subshell does not exist.
- Each subshell has $2l + 1$ orbitals. This means that all *ns* subshells contain a single s orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

Each principal shell has n subshells, and each subshell has $2l + 1$ orbitals.

Table 6.5.1: Values of n, l, and ml through n = 4

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

YouTube Video

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View this YouTube Video online

Magnetic Quantum Number (ml) & Spin Quantum Number (ms): Magnetic Quantum Number (ml) & Spin Quantum Number (ms) YouTube(opens in new window) [youtu.be] (opens in new window)

Summary

There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wavefunctions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wavefunctions have five important properties:

1. the wavefunction uses three variables (Cartesian axes *x*, *y*, and *z*) to describe the position of an electron;
2. the magnitude of the wavefunction is proportional to the intensity of the wave;
3. the probability of finding an electron at a given point is proportional to the square of the wavefunction at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot;
4. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wavefunction; and
5. each spatial distribution of the electron described by a wavefunction with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** n can be any positive integer; as n increases for an atom, the average distance of the electron from the nucleus also increases. All wavefunctions with the same value of n constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** l can have integral values between 0 and $n - 1$; it describes the shape of the electron distribution. Wavefunctions that have the same values of both n and l constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** m_l can have $2l + 1$ integral values, ranging from $-l$ to $+l$, and describes the orientation of the electron distribution. Each wavefunction with a given set of values of n, l, and m_l describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

Answers

Exercise 6.5.1: n=3 Shell Structure

three subshells; nine orbitals

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6.6: 3D Representation of Orbitals

Learning Objectives

- To understand the 3D representation of electronic orbitals

An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different **probabilities** of containing an electron.

One way of representing electron probability distributions was illustrated previously for the 1**s** orbital of hydrogen. Because Ψ^2 gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of Ψ^2 versus distance from the nucleus (**r**) is a plot of the **probability density**. The 1**s** orbital is spherically symmetrical, so the probability of finding a 1**s** electron at any given point depends **only** on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of **r**, the electron probability density is very small but **not** zero.

In contrast, we can calculate the **radial probability** (the probability of finding a 1s electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of **x** spherical shells of radius $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$,..., $\mathbf{r}_{x-1}$, $\mathbf{r}_x$. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (Figure $6.6.1a$), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at r = 0 (Figure $6.6.1b$), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure $6.6.1$. In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing r (Figure $6.6.1c$). Because the surface area of the spherical shells increases more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (Figure $6.6.1d$). Most important, when r is very small, the surface area of a spherical shell is so small that the **total** probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (Figure $6.6.1d$).

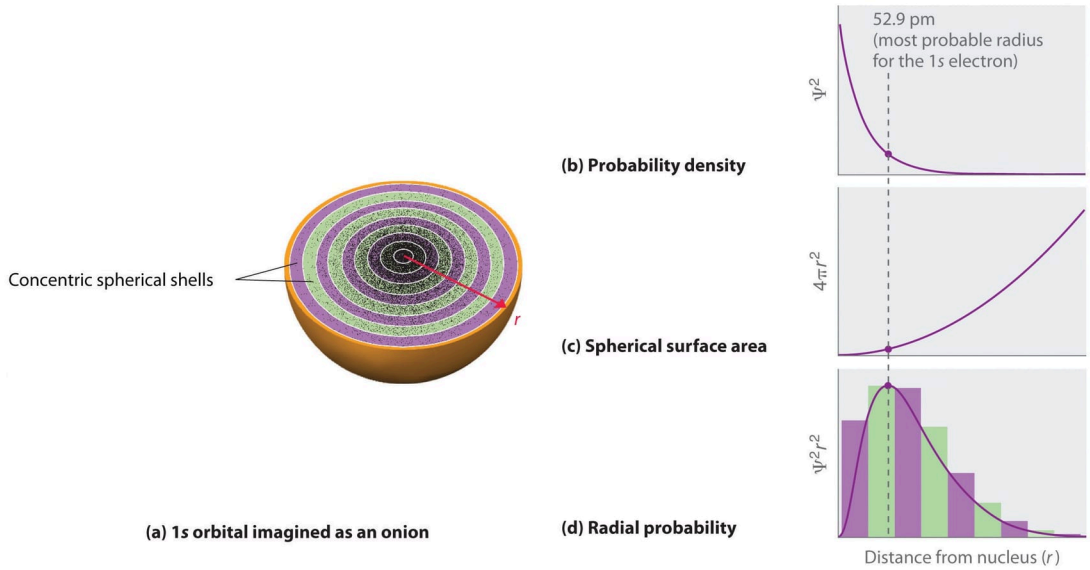


Figure $6.6.1$: Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at r = 0 and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi\mathbf{r}^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the **radial probability**) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at r = 0.529 Å (52.9 pm), which is exactly the radius calculated by Bohr for the **n** = 1 orbit. Thus the **most probable radius** obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 6.6.2 compares the electron probability densities for the hydrogen 1**s**, 2**s**, and 3**s** orbitals. Note that all three are spherically symmetrical. For the 2**s** and 3**s** orbitals, however (and for all other **s** orbitals as well), the electron probability density does not fall off smoothly with increasing r. Instead, a series of minima and maxima are observed in the radial probability plots (Figure 6.6.2*c*). The minima correspond to spherical **nodes** (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability. The existence of these nodes is a consequence of changes of wave **phase** in the wavefunction Ψ.

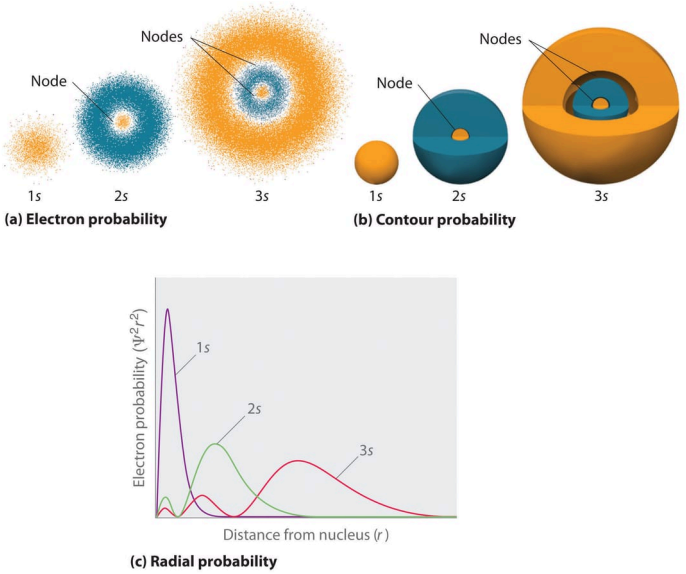


Figure 6.6.2: Probability Densities for the 1**s**, 2**s**, and 3**s** Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1**s**, 2**s**, and 3**s** orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (**r**) in all directions (radial probability), the most probable radius increases as **n** increases, but the 2**s** and 3**s** orbitals have regions of significant electron probability at small values of r.

s Orbitals (l=0)

Three things happen to **s** orbitals as **n** increases (Figure 6.6.2):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the **s** orbitals also become higher in energy as **n** increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1**s**, 2**s**, and 3**s** orbitals in part (b) in Figure 6.6.2. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2**s** and 3**s** orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals (l=1)

Only **s** orbitals are spherically symmetrical. As the value of **l** increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2**p** subshell has **l** = 1, with three values of $\mathbf{m_l}$ (–1, 0, and +1), there

are three 2**p** orbitals.

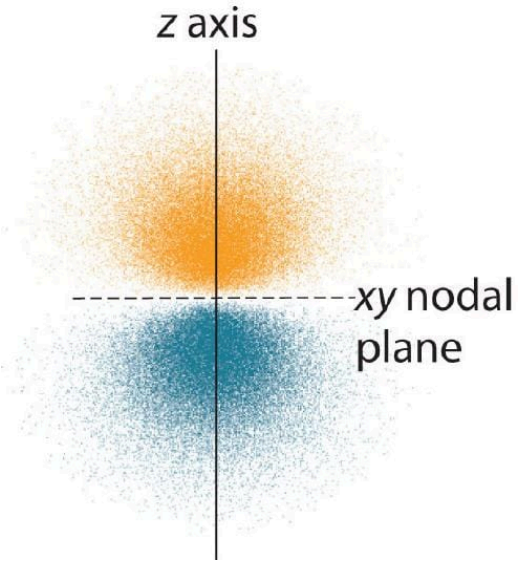


Figure 6.6.3: Electron Probability Distribution for a Hydrogen 2**p** Orbital. The nodal plane of zero electron density separates the two lobes of the 2**p** orbital. As in Figure 6.6.2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2**p** orbitals is shown in Figure 6.6.3. Because this orbital has two lobes of electron density arranged along the **z** axis, with an electron density of zero in the **xy** plane (i.e., the **xy** plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 6.6.4, the other two 2**p** orbitals have identical shapes, but they lie along the **x** axis ($2p_x$) and y axis ($2p_y$), respectively. Note that each **p** orbital has just one **nodal plane**. In each case, the phase of the wave function for each of the 2**p** orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the **phase** of the wave that describes the electron motion, **not** to positive or negative charges.

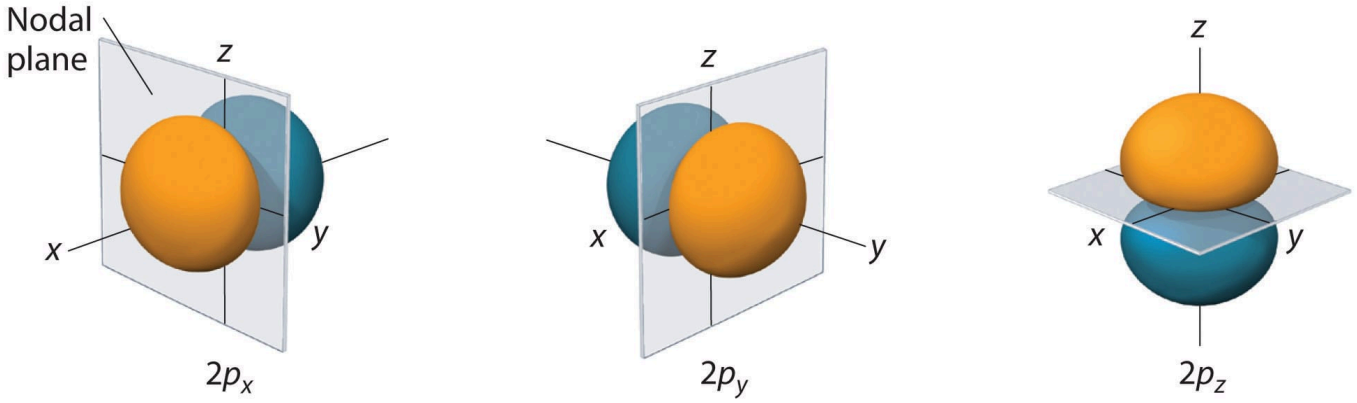


Figure 6.6.4 The Three Equivalent 2**p** Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the 2$\mathbf{p_x}$, 2$\mathbf{p_y}$, and 2$\mathbf{p_z}$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2**p** orbital. The phase of the wave function is positive (orange) in the region of space where **x**, **y**, or **z** is positive and negative (blue) where **x**, **y**, or **z** is negative. Just as with the **s** orbitals, the size and complexity of the **p** orbitals for any atom increase as the principal quantum number **n** increases. The shapes of the 90% probability surfaces of the 3**p**, 4**p**, and higher-energy **p** orbitals are, however, essentially the same as those shown in Figure 6.6.4.

d Orbitals (l=2)

Subshells with **l** = 2 have five **d** orbitals; the first principal shell to have a **d** subshell corresponds to **n** = 3. The five **d** orbitals have $\mathbf{m_l}$ values of −2, −1, 0, +1, and +2.

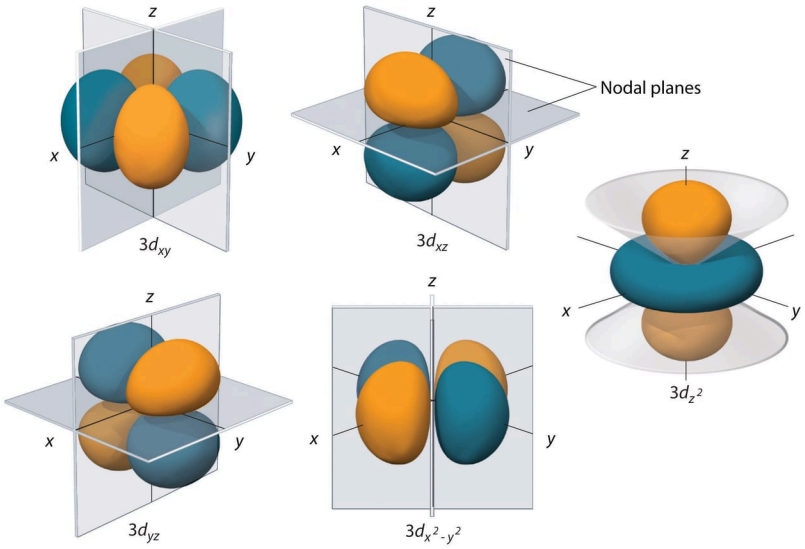


Figure 6.6.5: The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The 3 d orbitals can be broken down into 3 d x y, 3 d x z, 3 d y squared, 3 d x squared minus y squared, 3 d z squared.

The hydrogen 3d orbitals, shown in Figure 6.6.5, have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, \)3d_{xz}\), and $3d_{yz}$ orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the $3d_{x^2-y^2}$ orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure 6.6.5, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 6.6.5.

f Orbitals (l=3)

Principal shells with **n** = 4 can have subshells with **l** = 3 and $\mathbf{m_l}$ values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven **f** orbitals. Each **f** orbital has three nodal surfaces, so their shapes are complex. Because **f** orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of **l** are not discussed at all.

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or He^+).

The relative energies of the atomic orbitals with **n** ≤ 4 for a hydrogen atom are plotted in Figure 6.6.6; note that the orbital energies depend on **only** the principal quantum number **n**. Consequently, the energies of the 2**s** and 2**p** orbitals of hydrogen are the same; the energies of the 3**s**, 3**p**, and 3**d** orbitals are the same; and so forth. Quantum mechanics predicts that in the hydrogen

atom, all orbitals with the same value of **n** (e.g., the three 2**p** orbitals) are **degenerate**, meaning that they have the same energy. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are **4** orbitals with different electron density distributions in the **n** = 2 principal shell (one 2**s** and three 2**p** orbitals), **9** in the **n** = 3 principal shell, and **16** in the **n** = 4 principal shell.The different values of **l** and $\mathbf{m_l}$ for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. Figure $6.6.6$ shows that the energy levels become closer and closer together as the value of **n** increases, as expected because of the 1/$\mathbf{n}^2$ dependence of orbital energies.

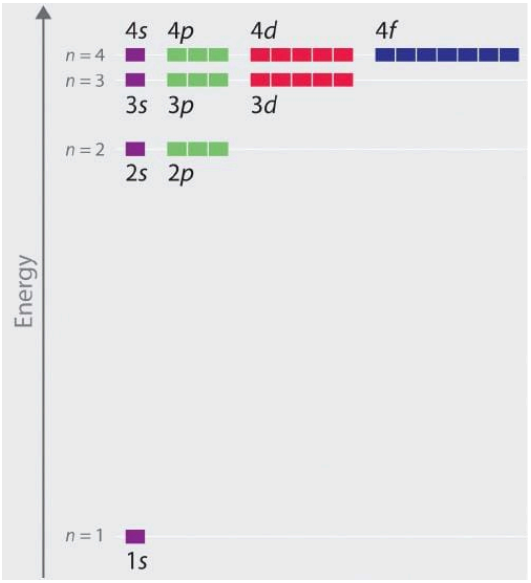


Figure $6.6.6$: Orbital Energy Level Diagram for the Hydrogen Atom with a single electron. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of **n**.

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation, which can be extended to other single-electron species by incorporating the nuclear charge Z (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2}Rhc \tag{6.6.1}$$

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n = 2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the p_x, p_y, and p_z orbitals, are degenerate.

Summary

The four chemically important types of atomic orbital correspond to values of $\ell = 0$, 1, 2, and 3. Orbitals with $\ell = 0$ are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of $n > 1$ and $ell = 0$ contain one or more nodes. Orbitals with $\ell = 1$ are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $\ell = 2$ are d orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with $\ell = 3$ are f orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**.

$$E = -\frac{Z^2}{n^2}Rhc$$

In atoms or ions with only a single electron, all orbitals with the same value of n have the same energy (they are degenerate), and the energies of the principal shells increase smoothly as n increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

Contributors and Attributions

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6.7: Many-Electron Atoms

Learning Objectives

- To write the electron configuration of any element and relate its electron configuration to its position in the periodic table.

The quantum mechanical model allowed us to determine the energies of the hydrogen atomic orbitals; now we would like to extend this to describe the electronic structure of every element in the Periodic Table. The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table; however, interactions between electrons make this process a bit more complicated than it sounds. All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion. Before demonstrating how to do this, however, we must introduce the concept of electron spin and the Pauli principle.

Orbitals and their Energies

Unlike in hydrogen-like atoms with only one electron, in multielectron atoms the values of quantum numbers *n and l* determine the energies of an orbital. The energies of the different orbitals for a typical multielectron atom are shown in Figure 6.7.1. Within a given principal shell of a multielectron atom, the orbital energies increase with increasing *l*. An *ns* orbital always lies below the corresponding *np* orbital, which in turn lies below the *nd* orbital.

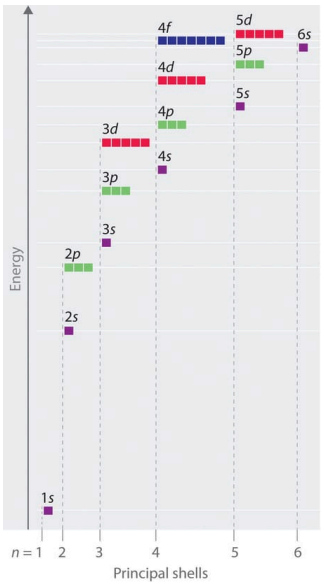


Figure 6.7.1: Orbital Energy Level Diagram for a Typical Multielectron Atom

These energy differences are caused by the effects of *shielding* and *penetration*, the extent to which a given orbital lies inside other filled orbitals. For example, an electron in the 2*s* orbital penetrates inside a filled 1*s* orbital more than an electron in a 2*p* orbital does. Since electrons, all being negatively charged, repel each other, an electron closer to the nucleus partially *shield*s an electron farther from the nucleus from the attractive effect of the positively charged nucleus. Hence in an atom with a filled 1*s* orbital, the effective nuclear charge (Z_{eff}) experienced by a 2*s* electron is greater than the Z_{eff} experienced by a 2*p* electron. Consequently, the 2*s* electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 6.7.1.

> Due to electron shielding, Z_{eff} increases more rapidly going across a row of the periodic table than going down a column.

Notice in Figure 6.7.1 that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3*d* orbitals in most atoms is actually *between* the energies of the 4*s* and the 4*p* orbitals.

Electron Spin: The Fourth Quantum Number

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers n, l, and m_l. Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called **electron spin**.

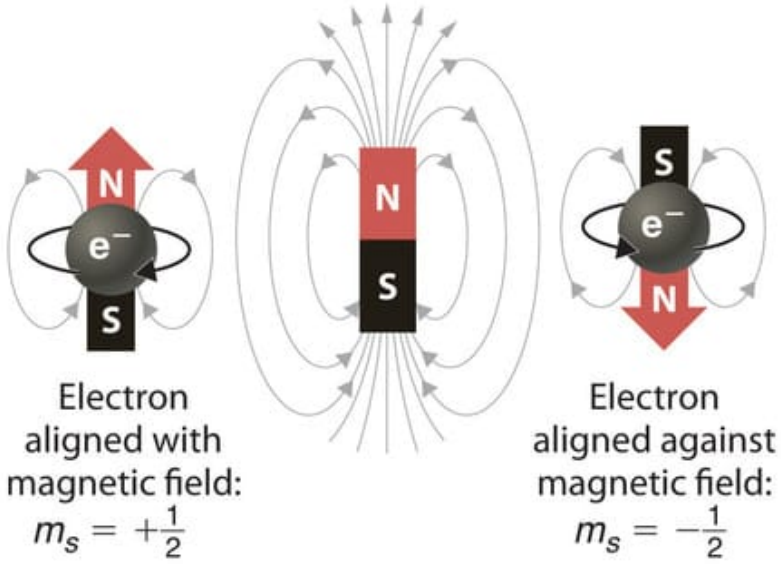


Figure 6.7.2: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure Figure 6.7.2). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated +½ (up) and –½ (down) to indicate that the two orientations are opposites; the subscript s is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

The Pauli Exclusion Principle

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion principle: *No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).*

By giving the values of *n*, *l*, and m_l, we also specify a particular orbital (e.g., 1s with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values (+½ or –½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which was originally based on the

physical and chemical properties of the known elements.

Example 6.7.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a $2p$ orbital and predict the maximum number of electrons the $2p$ subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A. List the quantum numbers (n, l, m_l) that correspond to an $n = 2p$ orbital. List all allowed combinations of (n, l, m_l).
B. Build on these combinations to list all the allowed combinations of (n, l, m_l, m_s).
C. Add together the number of combinations to predict the maximum number of electrons the $2p$ subshell can accommodate.

Solution:

A For a $2p$ orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l, (-l + 1),..., (l - 1), l$. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, –1).

B Because m_s is independent of the other quantum numbers and can have values of only +½ and –½, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, +½), (2, 1, 1, –½), (2, 1, 0, +½), (2, 1, 0, –½), (2, 1, –1, +½), and (2, 1, –1, –½).

C Hence the $2p$ subshell, which consists of three $2p$ orbitals ($2p_x$, $2p_y$, and $2p_z$), can contain a total of six electrons, two in each orbital.

Exercise 6.7.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a 6s orbital, and predict the total number of electrons it can contain.

Answer available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Magnetic Quantum Number (ml) & Spin Quantum Number (ms): Magnetic Quantum Number (ml) & Spin Quantum Number (ms), YouTube(opens in new window) [youtu.be] (opens in new window)

Summary

The arrangement of atoms in the periodic table arises from the lowest energy arrangement of electrons in the valence shell. In addition to the three quantum numbers (n, l, m_l) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the **electron spin** quantum number (m_s), which can have values of +½ or –½ for any electron,

corresponding to the two possible orientations of an electron in a magnetic field. The concept of electron spin has important consequences for chemistry because the **Pauli exclusion principle** implies that no orbital can contain more than two electrons (with opposite spin).

Answers

Exercise 6.7.1

(6, 0, 0, +½), (6, 0, 0, −½); two electrons

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6.8: Electron Configurations

Learning Objectives

- To understand the basics of adding electrons to atomic orbitals
- To understand the basics of the Aufbau principle

The electron configuration of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

The Aufbau Principle

We construct the periodic table by following the aufbau principle (from German, meaning "building up"). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 6.8.1, recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to $m_S = +½$, which is arbitrarily written first, and one with spin down ↓, corresponding to $m_S = –½$. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

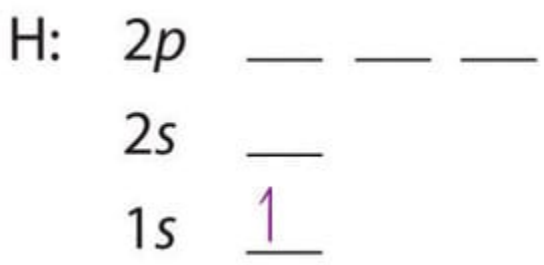
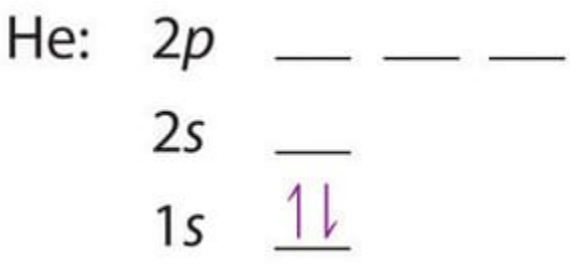


Figure 6.8.1: One electron in.

From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number *n* and their value of *l* (s, *p*, *d*, or *f*), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1s orbital, which is the orbital lowest in energy (Figure 6.8.1), and the electron configuration is written as $1s^1$ and read as "one-s-one."

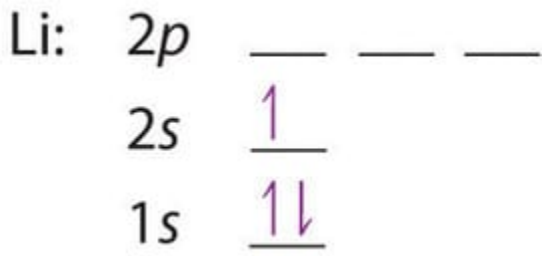
A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the 1s orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

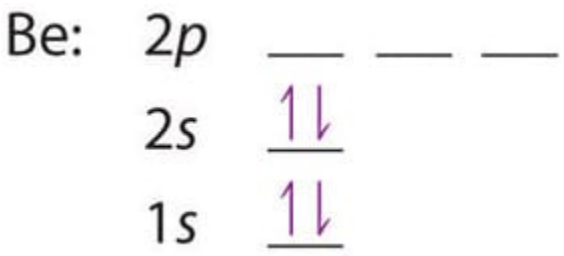
The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the 1s orbital can hold two of the

electrons with their spins paired; the third electron must enter a higher energy orbital. Figure 6.29 tells us that the next lowest energy orbital is 2s, so the orbital diagram for lithium is

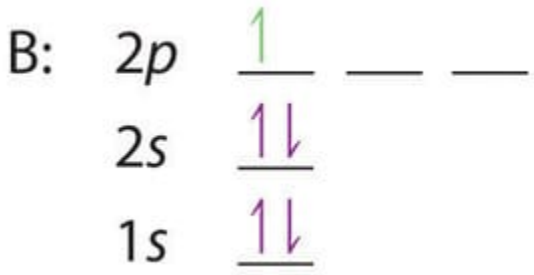


This electron configuration is written as $1s^2 2s^1$.

The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1s and 2s orbitals to achieve a $1s^2 2s^2$ electron configuration:

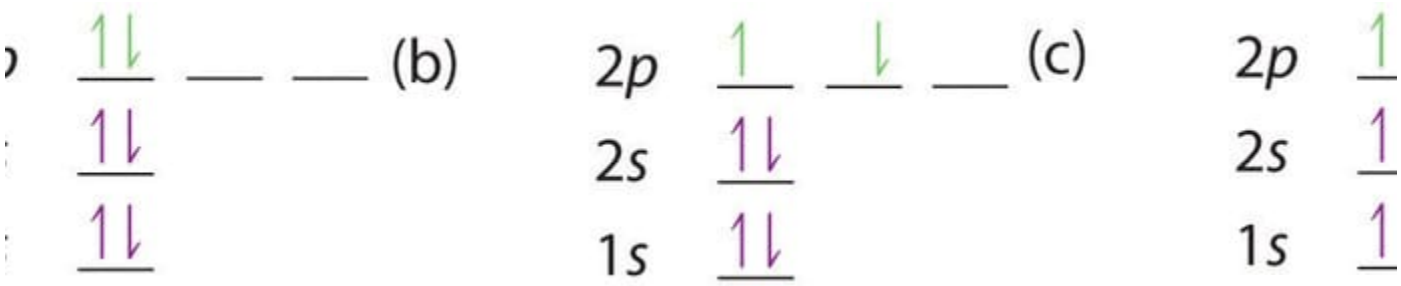


When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Because all three 2*p* orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2 2s^2 2p^1$:



Boron has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and one electron in the 2 p orbital.

At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2*p* orbital that already has an electron, or should it go in one of the empty 2*p* orbitals? If it goes in an empty 2*p* orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the 2*p* orbitals are degenerate?



the sixth electron should go, a) paired
e 2 p orbital, b) unpaired with the lone
vnward, and c) unpaired with the lone
electron

Because of electron-electron interactions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates **Hund's rule** (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

When we get to nitrogen (Z = 7, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

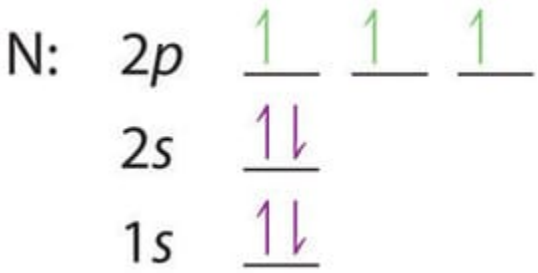
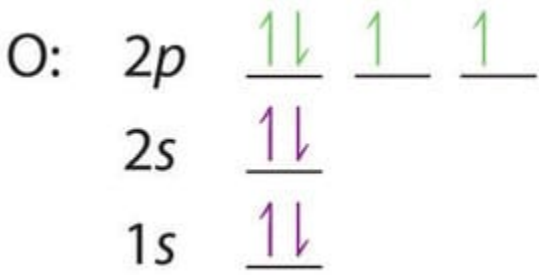


Figure 6.8.1: Copy and Paste Caption here. (Copyright; author via source)

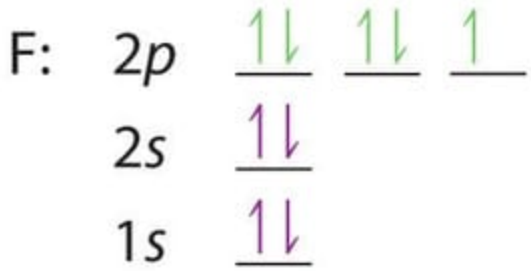
with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

At oxygen, with Z = 8 and eight electrons, we have no choice. One electron must be paired with another in one of the 2p orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration. Because all the 2p orbitals are degenerate, it doesn't matter which one has the pair of electrons.



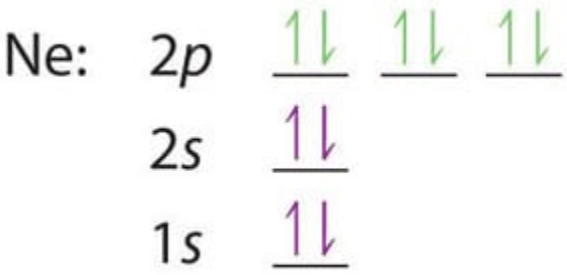
Oxygen has one electron pair in the 1 s orbital, one electron pair in the 2 s pair, and one electron pair, and 2 unpaired electrons in the 2 p orbitals.

Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:



Fluorine has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and 2 electrons pairs with one unpaired electron in the 2 p orbital.

When we reach neon, with Z = 10, we have filled the 2p subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:



Neon has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and 3 electron pairs in the 2 p orbital.

Notice that for neon, as for helium, all the orbitals through the 2p level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

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Valence Electrons

As we continue through the periodic table in this way, writing the electron configurations of larger and larger atoms, it becomes tedious to keep copying the configurations of the filled inner subshells. In practice, chemists simplify the notation by using a bracketed noble gas symbol to represent the configuration of the noble gas from the preceding row because all the orbitals in a noble gas are filled. For example, [Ne] represents the $1s^2 2s^2 2p^6$ electron configuration of neon (Z = 10), so the electron configuration of sodium, with Z = 11, which is $1s^2 2s^2 2p^6 3s^1$, is written as [Ne]$3s^1$:

Electron Configuration of Neon and Sodium

Neon	Z = 10	$1s^2 2s^2 2p^6$
Sodium	Z = 11	$1s^2 2s^2 2p^6$**3**s^1 = [Ne]**3**s^1

Because electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, they are rarely involved in chemical reactions. This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, which are called the **valence electrons**. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium and lithium, we have:

Electron Configuration of Sodium and Lithium

Sodium	**$1s^2 2s^2 2p^6 3s^1$ = [Ne]$3s^1$**
Lithium	$1s^2 2s^1$ = [He]$2s^1$

It is readily apparent that both sodium and lithium have one s electron in their valence shell. We would therefore predict that sodium and lithium have very similar chemistry, which is indeed the case.

As we continue to build the eight elements of period 3, the 3*s* and 3*p* orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration [Ne]$3s^2 3p^6$, corresponding to a filled valence shell.

Example 6.8.1: Electronic Configuration of Phosphorus

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, Z = 15. What is its valence electron configuration?

Given: atomic number

Asked for: orbital diagram and valence electron configuration for phosphorus

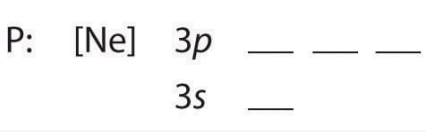
Strategy:

A. Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.
B. Referring to Figure 6.8.1, draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.
C. Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

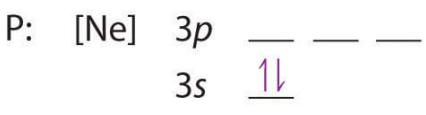
Solution:

A Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

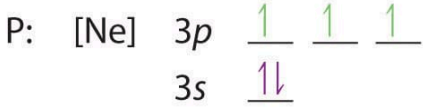
B The additional five electrons are placed in the next available orbitals, which Figure 6.8.1 tells us are the 3*s* and 3*p* orbitals:



Because the 3*s* orbital is lower in energy than the 3*p* orbitals, we fill it first:



Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:



The electron configuration is [Ne]$3s^2 3p^3$.

C We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^2 3p^3$.

Exercise 6.8.1

Draw an orbital diagram and use it to derive the electron configuration of chlorine, Z = 17. What is its valence electron configuration?

Answer available at the end of this section.

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The general order in which orbitals are filled is depicted in Figure 6.8.2. Subshells corresponding to each value of n are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4s orbital is filled prior to the 3d orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is [Ar]$4s^1$, and the configuration of calcium is [Ar]$4s^2$. Five 3d orbitals are filled by the next 10 elements, the transition metals, followed by three 4p orbitals. Notice that the last member of this row is the noble gas krypton (Z = 36), [Ar]$4s^2 3d^{10} 4p^6$ = [Kr], which has filled 4s, 3d, and 4p orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5s, 4d, and 5p orbitals are filled sequentially.

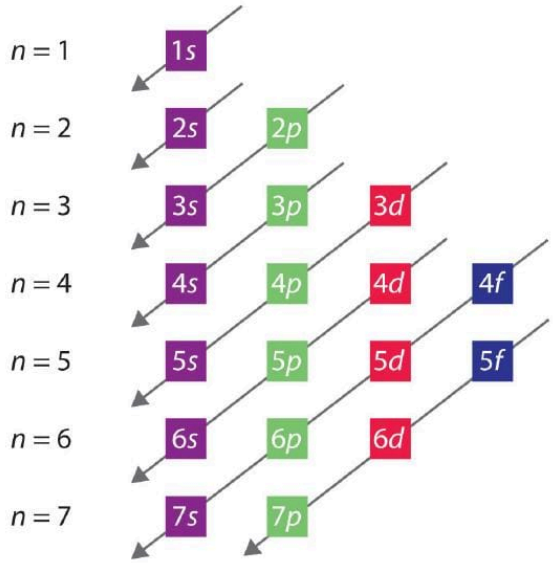


Figure 6.8.2: Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.

The sixth row of the periodic table will be different from the preceding two because the 4*f* orbitals, which can hold 14 electrons, are filled between the 6s and the 5*d* orbitals. The elements that contain 4*f* orbitals in their valence shell are the lanthanides. When the 6*p* orbitals are finally filled, we have reached the next noble gas, radon (Z = 86), [Xe]$6s^2 4f^{14} 5d^{10} 6p^6$ = [Rn]. In the last row, the 5*f* orbitals are filled between the 7s and the 6*d* orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

Example 6.8.2: Electron Configuration of Mercury

Write the electron configuration of mercury (Z = 80), showing all the inner orbitals.

Given: atomic number

Asked for: complete electron configuration

Strategy:

Using the orbital diagram in Figure 6.8.1 and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

Solution:

By placing the electrons in orbitals following the order shown in Figure 6.8.2 and using the periodic table as a guide, we obtain

Solution to Example 6.8.2

$1s^2$	row 1	2 electrons
$2s^2 2p^6$	row 2	8 electrons
$3s^2 3p^6$	row 3	8 electrons
$4s^2 3d^{10} 4p^6$	row 4	18 electrons
$5s^2 4d^{10} 5p^6$	row 5	18 electrons

$1s^2$	row 1	2 electrons
	row 1–5	54 electrons

After filling the first five rows, we still have 80 – 54 = 26 more electrons to accommodate. According to Figure 6.8.2, we need to fill the 6s (2 electrons), 4*f* (14 electrons), and 5*d* (10 electrons) orbitals. The result is mercury's electron configuration:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} = Hg = [Xe]6s^2 4f^{14} 5d^{10}$$

with a filled 5*d* subshell, a $6s^2 4f^{14} 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

Exercise 6.8.2: Electron Configuration of Flerovium

Although element 114 is not stable enough to occur in nature, atoms of element 114 were created for the first time in a nuclear reactor in 1998 by a team of Russian and American scientists. The element is named after the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research in Dubna, Russia, where the element was discovered. The name of the laboratory, in turn, honors the Russian physicist Georgy Flyorov. Write the complete electron configuration for element 114.

Answer available at the end of this section.

The electron configurations of the elements are presented in Figure 6.8.2, which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted by Figure 6.8.1. Some of these anomalies occur as the 3*d* orbitals are filled. For example, the observed ground state electron configuration of chromium is $[Ar]4s^1 3d^5$ rather than the predicted $[Ar]4s^2 3d^4$. Similarly, the observed electron configuration of copper is $[Ar]4s^1 3d^{10}$ instead of $[Ar]s^2 3d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled (ns^1, np^3, nd^5, nf^7) or filled (ns^2, np^6, nd^{10}, nf^{14}) subshell. (In fact, this "special stability" is really another consequence of the *instability* caused by pairing an electron with another in the same orbital, as illustrated by Hund's rule.) Given the small differences between higher energy levels, this added stability is enough to shift an electron from one orbital to another. In heavier elements, other more complex effects can also be important, leading to many additional anomalies. For example, cerium has an electron configuration of $[Xe]6s^2 4f^1 5d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

Additional stability is associated with half-filled or filled subshells.

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Summary

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the

lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**.

Answers

Exercise 6.8.1

[Ne]$3s^2 3p^5$; $3s^2 3p^5$

Exercise 6.8.2**: Electron Configuration of Flerovium**

$s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^2$

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6.9: Electron Configurations and the Periodic Table

Learning Objectives

- To correlate the arrangement of atoms in the periodic table results in blocks corresponding to filling of the *ns*, *np*, *nd*, and *nf* orbitals

As you have learned, the electron configurations of the elements explain the otherwise peculiar shape of the periodic table. Although the table was originally organized on the basis of physical and chemical similarities between the elements within groups, these similarities are ultimately attributable to orbital energy levels and the Pauli principle, which cause the individual subshells to be filled in a particular order. As a result, the periodic table can be divided into "blocks" corresponding to the type of subshell that is being filled, as illustrated in Figure 6.9.1. For example, the two columns on the left, known as the s block, consist of elements in which the *ns* orbitals are being filled. The six columns on the right, elements in which the *np* orbitals are being filled, constitute the *p* block. In between are the 10 columns of the *d* block, elements in which the $(n - 1)d$ orbitals are filled. At the bottom lie the 14 columns of the *f* block, elements in which the $(n - 2)f$ orbitals are filled. Because two electrons can be accommodated per orbital, the number of columns in each block is the same as the maximum electron capacity of the subshell: 2 for *ns*, 6 for *np*, 10 for $(n - 1)d$, and 14 for $(n - 2)f$. Within each column, each element has the same valence electron configuration—for example, ns^1 (group 1) or ns^2np^1 (group 13). As you will see, this is reflected in important similarities in the chemical reactivity and the bonding for the elements in each column.

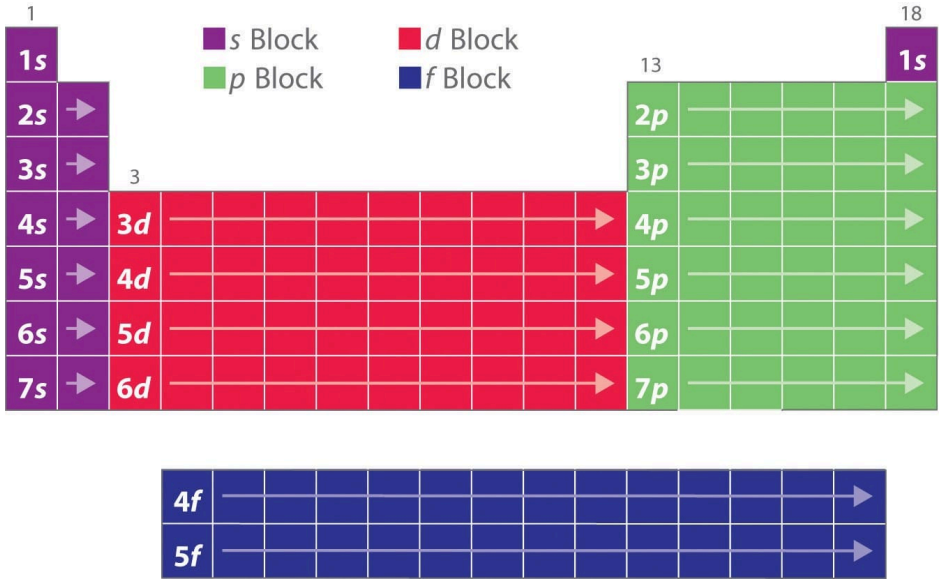


Figure 6.9.1: The Periodic Table, Showing How the Elements Are Grouped According to the Kind of Subshell (*s*, *p*, *d*, *f*) Being Filled with Electrons in the Valence Shell of Each Element. The electron configurations of the elements are in Figure 6.9.2.

Because each orbital can have a maximum of 2 electrons, there are 2 columns in the *s* block, 6 columns in the *p* block, 10 columns in the *d* block, and 14 columns in the *f* block.

Hydrogen and helium are placed somewhat arbitrarily. Although hydrogen is not an alkali metal, its $1s^1$ electron configuration suggests a similarity to lithium ($[He]2s^1$) and the other elements in the first column. Although helium, with a filled *ns* subshell, should be similar chemically to other elements with an ns^2 electron configuration, the closed principal shell dominates its chemistry, justifying its placement above neon on the right.

Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	$1s^1$	37	Rb	[Kr]$5s^1$	73	Ta	[Xe]$6s^24f^{14}5d^3$
2	He	$1s^2$	38	Sr	[Kr]$5s^2$	74	W	[Xe]$6s^24f^{14}5d^4$
3	Li	[He]$2s^1$	39	Y	[Kr]$5s^24d^1$	75	Re	[Xe]$6s^24f^{14}5d^5$
4	Be	[He]$2s^2$	40	Zr	[Kr]$5s^24d^2$	76	Os	[Xe]$6s^24f^{14}5d^6$
5	B	[He]$2s^22p^1$	41	Nb	[Kr]$5s^14d^4$	77	Ir	[Xe]$6s^24f^{14}5d^7$
6	C	[He]$2s^22p^2$	42	Mo	[Kr]$5s^14d^5$	78	Pt	[Xe]$6s^14f^{14}5d^9$
7	N	[He]$2s^22p^3$	43	Tc	[Kr]$5s^24d^5$	79	Au	[Xe]$6s^14f^{14}5d^{10}$
8	O	[He]$2s^22p^4$	44	Ru	[Kr]$5s^14d^7$	80	Hg	[Xe]$6s^24f^{14}5d^{10}$
9	F	[He]$2s^22p^5$	45	Rh	[Kr]$5s^14d^8$	81	Tl	[Xe]$6s^24f^{14}5d^{10}6p^1$
10	Ne	[He]$2s^22p^6$	46	Pd	[Kr]$4d^{10}$	82	Pb	[Xe]$6s^24f^{14}5d^{10}6p^2$
11	Na	[Ne]$3s^1$	47	Ag	[Kr]$5s^14d^{10}$	83	Bi	[Xe]$6s^24f^{14}5d^{10}6p^3$
12	Mg	[Ne]$3s^2$	48	Cd	[Kr]$5s^24d^{10}$	84	Po	[Xe]$6s^24f^{14}5d^{10}6p^4$
13	Al	[Ne]$3s^23p^1$	49	In	[Kr]$5s^24d^{10}5p^1$	85	At	[Xe]$6s^24f^{14}5d^{10}6p^5$
14	Si	[Ne]$3s^23p^2$	50	Sn	[Kr]$5s^24d^{10}5p^2$	86	Rn	[Xe]$6s^24f^{14}5d^{10}6p^6$
15	P	[Ne]$3s^23p^3$	51	Sb	[Kr]$5s^24d^{10}5p^3$	87	Fr	[Rn]$7s^1$
16	S	[Ne]$3s^23p^4$	52	Te	[Kr]$5s^24d^{10}5p^4$	88	Ra	[Rn]$7s^2$
17	Cl	[Ne]$3s^23p^5$	53	I	[Kr]$5s^24d^{10}5p^5$	89	Ac	[Rn]$7s^26d^1$
18	Ar	[Ne]$3s^23p^6$	54	Xe	[Kr]$5s^24d^{10}5p^6$	90	Th	[Rn]$7s^26d^2$
19	K	[Ar]$4s^1$	55	Cs	[Xe]$6s^1$	91	Pa	[Rn]$7s^25f^26d^1$
20	Ca	[Ar]$4s^2$	56	Ba	[Xe]$6s^2$	92	U	[Rn]$7s^25f^36d^1$
21	Sc	[Ar]$4s^23d^1$	57	La	[Xe]$6s^25d^1$	93	Np	[Rn]$7s^25f^46d^1$
22	Ti	[Ar]$4s^23d^2$	58	Ce	[Xe]$6s^24f^15d^1$	94	Pu	[Rn]$7s^25f^6$
23	V	[Ar]$4s^23d^3$	59	Pr	[Xe]$6s^24f^3$	95	Am	[Rn]$7s^25f^7$
24	Cr	[Ar]$4s^13d^5$	60	Nd	[Xe]$6s^24f^4$	96	Cm	[Rn]$7s^25f^76d^1$
25	Mn	[Ar]$4s^23d^5$	61	Pm	[Xe]$6s^24f^5$	97	Bk	[Rn]$7s^25f^9$
26	Fe	[Ar]$4s^23d^6$	62	Sm	[Xe]$6s^24f^6$	98	Cf	[Rn]$7s^25f^{10}$
27	Co	[Ar]$4s^23d^7$	63	Eu	[Xe]$6s^24f^7$	99	Es	[Rn]$7s^25f^{11}$
28	Ni	[Ar]$4s^23d^8$	64	Gd	[Xe]$6s^24f^75d^1$	100	Fm	[Rn]$7s^25f^{12}$
29	Cu	[Ar]$4s^13d^{10}$	65	Tb	[Xe]$6s^24f^9$	101	Md	[Rn]$7s^25f^{13}$
30	Zn	[Ar]$4s^23d^{10}$	66	Dy	[Xe]$6s^24f^{10}$	102	No	[Rn]$7s^25f^{14}$
31	Ga	[Ar]$4s^23d^{10}4p^1$	67	Ho	[Xe]$6s^24f^{11}$	103	Lr	[Rn]$7s^25f^{14}6d^1$
32	Ge	[Ar]$4s^23d^{10}4p^2$	68	Er	[Xe]$6s^24f^{12}$	104	Rf	[Rn]$7s^25f^{14}6d^2$
33	As	[Ar]$4s^23d^{10}4p^3$	69	Tm	[Xe]$6s^24f^{13}$	105	Db	[Rn]$7s^25f^{14}6d^3$
34	Se	[Ar]$4s^23d^{10}4p^4$	70	Yb	[Xe]$6s^24f^{14}$	106	Sg	[Rn]$7s^25f^{14}6d^4$
35	Br	[Ar]$4s^23d^{10}4p^5$	71	Lu	[Xe]$6s^24f^{14}5d^1$	107	Bh	[Rn]$7s^25f^{14}6d^5$
36	Kr	[Ar]$4s^23d^{10}4p^6$	72	Hf	[Xe]$6s^24f^{14}5d^2$	108	Hs	[Rn]$7s^25f^{14}6d^6$
						109	Mt	[Rn]$7s^25f^{14}6d^7$
						110	Ds	[Rn]$7s^25f^{14}6d^8$
						111	Rg	[Rn]$7s^25f^{14}6d^{10}$

Figure 6.9.2: Electron Configurations of the Elements. The electron configurations of elements indicated in red are exceptions due to the added stability associated with half-filled and filled subshells. The electron configurations of the elements indicated in blue are also anomalous, but the reasons for the observed configurations are more complex. For elements after No, the electron configurations are tentative.

Example 6.9.1

Use the periodic table to predict the valence electron configuration of all the elements of group 2 (beryllium, magnesium, calcium, strontium, barium, and radium).

Given: series of elements

Asked for: valence electron configurations

Strategy:

A. Identify the block in the periodic table to which the group 2 elements belong. Locate the nearest noble gas preceding each element and identify the principal quantum number of the valence shell of each element.
B. Write the valence electron configuration of each element by first indicating the filled inner shells using the symbol for the nearest preceding noble gas and then listing the principal quantum number of its valence shell, its valence orbitals, and the number of valence electrons in each orbital as superscripts.

Solution:

A The group 2 elements are in the s block of the periodic table, and as group 2 elements, they all have two valence electrons. Beginning with beryllium, we see that its nearest preceding noble gas is helium and that the principal quantum number of its valence shell is $n = 2$.

B Thus beryllium has an $[He]s^2$ electron configuration. The next element down, magnesium, is expected to have exactly the same arrangement of electrons in the $n = 3$ principal shell: $[Ne]s^2$. By extrapolation, we expect all the group 2 elements to have an ns^2 electron configuration.

Exercise 6.9.1

Use the periodic table to predict the characteristic valence electron configuration of the halogens in group 17.

Answer available at the end of this section.

Summary

The arrangement of atoms in the periodic table results in blocks corresponding to filling of the *ns*, *np*, *nd*, and *nf* orbitals to produce the distinctive chemical properties of the elements in the s **block**, *p* **block**, *d* **block**, and *f* **block**, respectively.

Answers

Exercise 6.9.1

All have an ns^2np^5 electron configuration, one electron short of a noble gas electron configuration. (Note that the heavier halogens also have filled $(n - 1)d^{10}$ subshells, as well as an $(n - 2)f^{14}$ subshell for Rn; these do not, however, affect their chemistry in any significant way.

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6.E: Electronic Structure of Atoms (Exercises)

6.1: The Wave Nature of Light

Conceptual Problems

1. What are the characteristics of a wave? What is the relationship between electromagnetic radiation and wave energy?
2. At constant wavelength, what effect does increasing the frequency of a wave have on its speed? its amplitude?
3. List the following forms of electromagnetic radiation in order of increasing wavelength: x-rays, radio waves, infrared waves, microwaves, ultraviolet waves, visible waves, and gamma rays. List them in order of increasing frequency. Which has the highest energy?
4. A large industry is centered on developing skin-care products, such as suntan lotions and cosmetics, that cannot be penetrated by ultraviolet radiation. How does the wavelength of visible light compare with the wavelength of ultraviolet light? How does the energy of visible light compare with the energy of ultraviolet light? Why is this industry focused on blocking ultraviolet light rather than visible light?

Numerical Problems

1. The human eye is sensitive to what fraction of the electromagnetic spectrum, assuming a typical spectral range of 10^{4} to 10^{20} Hz? If we came from the planet Krypton and had x-ray vision (i.e., if our eyes were sensitive to x-rays in addition to visible light), how would this fraction be changed?

2. What is the frequency in megahertz corresponding to each wavelength?

    1. 755 m
    2. 6.73 nm
    3. 1.77×10^{3} km
    4. 9.88 Å
    5. 3.7×10^{-10} m

3. What is the frequency in megahertz corresponding to each wavelength?

    1. 5.8×10^{-7} m
    2. 2.3 Å
    3. 8.6×10^{7} m
    4. 6.2 mm
    5. 3.7 nm

4. Line spectra are also observed for molecular species. Given the following characteristic wavelengths for each species, identify the spectral region (ultraviolet, visible, etc.) in which the following line spectra will occur. Given 1.00 mol of each compound and the wavelength of absorbed or emitted light, how much energy does this correspond to?

    1. NH_3, 1.0×10^{-2} m
    2. CH_3CH_2OH, 9.0 μm
    3. Mo atom, 7.1 Å

5. What is the speed of a wave in meters per second that has a wavelength of 1250 m and a frequency of 2.36×10^{5} s^{-1}?

6. A wave travels at 3.70 m/s with a frequency of 4.599×10^{7} Hz and an amplitude of 1.0 m. What is its wavelength in nanometers?

7. An AM radio station broadcasts with a wavelength of 248.0 m. What is the broadcast frequency of the station in kilohertz?

An AM station has a broadcast range of 92.6 MHz. What is the corresponding wavelength range in meters for this reception?

8. An FM radio station broadcasts with a wavelength of 3.21 m. What is the broadcast frequency of the station in megahertz? An FM radio typically has a broadcast range of 82–112 MHz. What is the corresponding wavelength range in meters for this reception?

9. A microwave oven operates at a frequency of approximately 2450 MHz. What is the corresponding wavelength? Water, with its polar molecules, absorbs electromagnetic radiation primarily in the infrared portion of the spectrum. Given this fact, why are microwave ovens used for cooking food?

6.2: Quantized Energy and Photons

Conceptual Problems

1. Describe the relationship between the energy of a photon and its frequency.
2. How was the ultraviolet catastrophe explained?
3. If electromagnetic radiation with a continuous range of frequencies above the threshold frequency of a metal is allowed to strike a metal surface, is the kinetic energy of the ejected electrons continuous or quantized? Explain your answer.
4. The vibrational energy of a plucked guitar string is said to be quantized. What do we mean by this? Are the sounds emitted from the 88 keys on a piano also quantized?
5. Which of the following exhibit quantized behavior: a human voice, the speed of a car, a harp, the colors of light, automobile tire sizes, waves from a speedboat?

Conceptual Answers

1. The energy of a photon is directly proportional to the frequency of the electromagnetic radiation.

2.
3.
4.

5. Quantized: harp, tire size, speedboat waves; continuous: human voice, colors of light, car speed.

Numerical Problems

1. What is the energy of a photon of light with each wavelength? To which region of the electromagnetic spectrum does each wavelength belong?

    1. 4.33×10^{5} m
    2. 0.065 nm
    3. 786 pm

2. How much energy is contained in each of the following? To which region of the electromagnetic spectrum does each wavelength belong?

    1. 250 photons with a wavelength of 3.0 m
    2. 4.2×10^{6} photons with a wavelength of 92 μm
    3. 1.78×10^{22} photons with a wavelength of 2.1 Å

3. A 6.023×10^{23} photons are found to have an energy of 225 kJ. What is the wavelength of the radiation?

4. Use the data in Table 2.1.1 to calculate how much more energetic a single gamma-ray photon is than a radio-wave photon. How many photons from a radio source operating at a frequency of 8×10^{5} Hz would be required to provide the same amount of energy as a single gamma-ray photon with a frequency of 3×10^{19} Hz?

5. Use the data in Table 2.1.1 to calculate how much more energetic a single x-ray photon is than a photon of ultraviolet light.

6. A radio station has a transmitter that broadcasts at a frequency of 100.7 MHz with a power output of 50 kW. Given that 1 W = 1 J/s, how many photons are emitted by the transmitter each second?

Numerical Answers

1. 1. 4.59×10^{-31} J/photon, radio
   2. 3.1×10^{-15} J/photon, gamma ray
   3. 2.53×10^{-16} J/photon, gamma ray
2.

3. 532 nm

6.3: Line Spectra and the Bohr Model

Conceptual Problems

1. Is the spectrum of the light emitted by isolated atoms of an element discrete or continuous? How do these spectra differ from those obtained by heating a bulk sample of a solid element? Explain your answers.

2. Explain why each element has a characteristic emission and absorption spectra. If spectral emissions had been found to be continuous rather than discrete, what would have been the implications for Bohr's model of the atom?

3. Explain the differences between a ground state and an excited state. Describe what happens in the spectrum of a species when an electron moves from a ground state to an excited state. What happens in the spectrum when the electron falls from an excited state to a ground state?

4. What phenomenon causes a neon sign to have a characteristic color? If the emission spectrum of an element is constant, why do some neon signs have more than one color?

5. How is light from a laser different from the light emitted by a light source such as a light bulb? Describe how a laser produces light.

Numerical Problems

1. Using a Bohr model and the transition from $n = 2$ to $n = 3$ in an atom with a single electron, describe the mathematical relationship between an emission spectrum and an absorption spectrum. What is the energy of this transition? What does the sign of the energy value represent in this case? What range of light is associated with this transition?

2. If a hydrogen atom is excited from an $n = 1$ state to an $n = 3$ state, how much energy does this correspond to? Is this an absorption or an emission? What is the wavelength of the photon involved in this process? To what region of the electromagnetic spectrum does this correspond?

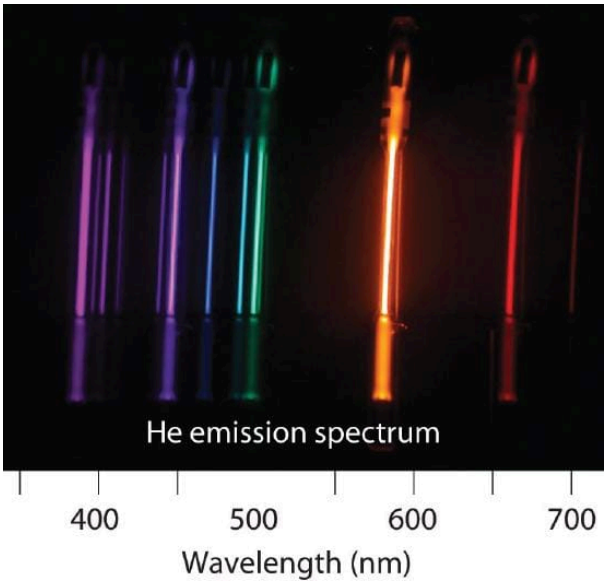
3. The hydrogen atom emits a photon with a 486 nm wavelength, corresponding to an electron decaying from the $n = 4$ level to which level? What is the color of the emission?

4. An electron in a hydrogen atom can decay from the $n = 3$ level to $n = 2$ level. What is the color of the emitted light? What is the energy of this transition?

5. Calculate the wavelength and energy of the photon that gives rise to the third line in order of increasing energy in the Lyman series in the emission spectrum of hydrogen. In what region of the spectrum does this wavelength occur? Describe qualitatively what the absorption spectrum looks like.

6. The wavelength of one of the lines in the Lyman series of hydrogen is 121 nm. In what region of the spectrum does this occur? To which electronic transition does this correspond?

7. The emission spectrum of helium is shown. Estimate what change in energy (ΔE) gives rise to each line?



8. Removing an electron from solid potassium requires 222 kJ/mol. Would you expect to observe a photoelectric effect for potassium using a photon of blue light (λ = 485 nm)? What is the longest wavelength of energy capable of ejecting an electron from potassium? What is the corresponding color of light of this wavelength?

9. The binding energy of an electron is the energy needed to remove an electron from its lowest energy state. According to Bohr's postulates, calculate the binding energy of an electron in a hydrogen atom. There are 6.02×10^{23} atoms in 1g of hydrogen atoms What wavelength in nanometers is required to remove such an electron from one hydrogen atom?

10. As a radio astronomer, you have observed spectral lines for hydrogen corresponding to a state with n = 320, and you would like to produce these lines in the laboratory. Is this feasible? Why or why not?

Numerical Answers

1. 656 nm; red light
2.
3. n = 2, blue-green light
4.
5. 97.2 nm, 2.04×10^{-18} J/photon, ultraviolet light, absorption spectrum is a single dark line at a wavelength of 97.2 nm
6.
7. Violet: 390 nm, 307 kJ/mol photons; Blue-purple: 440 nm, 272 kJ/mol photons; Blue-green: 500 nm, 239 kJ/mol photons; Orange: 580 nm, 206 kJ/mol photons; Red: 650 nm, 184 kJ/mol photons
8.
9. 1313 kJ/mol, $\lambda \leq$ 91.1 nm

6.4: The Wave Behavior of Matter

Conceptual Problems

1. Explain what is meant by each term and illustrate with a sketch:

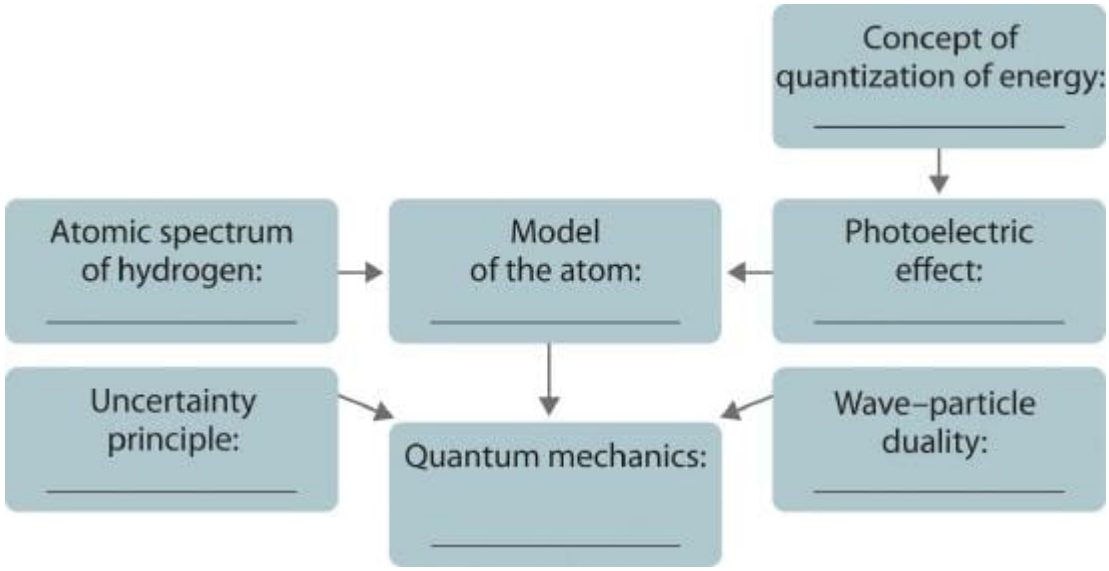
    1. standing wave
    2. fundamental
    3. overtone
    4. node

2. How does Einstein's theory of relativity illustrate the wave–particle duality of light? What properties of light can be explained by a wave model? What properties can be explained by a particle model?

3. In the modern theory of the electronic structure of the atom, which of de Broglie's ideas have been retained? Which proved to be incorrect?

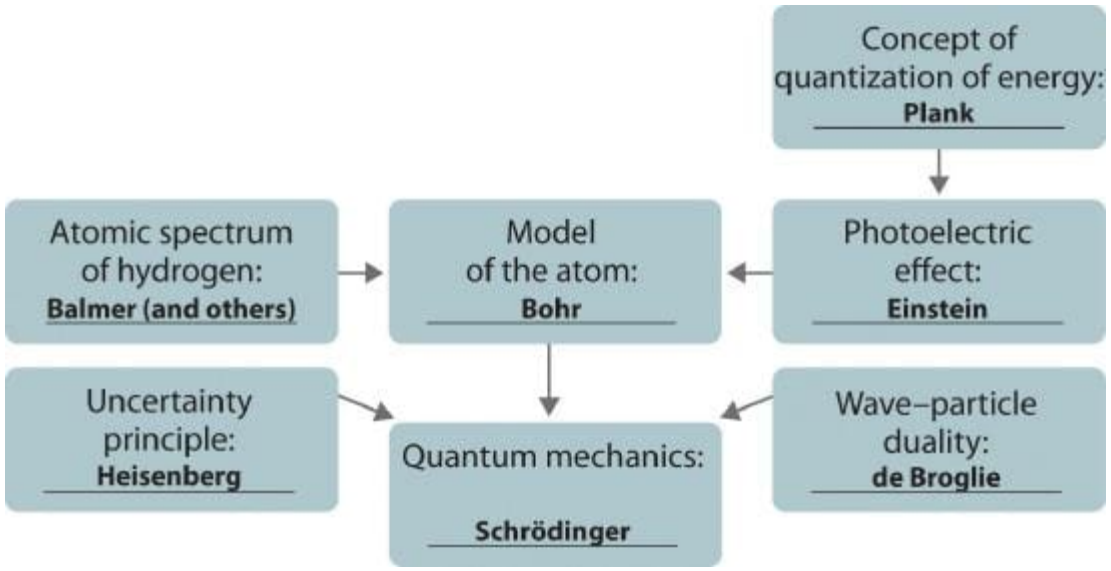
4. According to Bohr, what is the relationship between an atomic orbit and the energy of an electron in that orbit? Is Bohr's model of the atom consistent with Heisenberg's uncertainty principle? Explain your answer.

5. The development of ideas frequently builds on the work of predecessors. Complete the following chart by filling in the names of those responsible for each theory shown.



Conceptual Answer

1.
2.
3.
4.

5. 

Numerical Problems

1. How much heat is generated by shining a carbon dioxide laser with a wavelength of 1.065 μm on a 68.95 kg sample of water if 1.000 mol of photons is absorbed and converted to heat? Is this enough heat to raise the temperature of the water by 4°C?

2. Show the mathematical relationship between energy and mass and between wavelength and mass. What is the effect of doubling the

    1. mass of an object on its energy?
    2. mass of an object on its wavelength?
    3. frequency on its mass?

3. What is the de Broglie wavelength of a 39 g bullet traveling at 1020 m/s ± 10 m/s? What is the minimum uncertainty in the bullet's position?

4. What is the de Broglie wavelength of a 6800 tn aircraft carrier traveling at 18 ± 0.1 knots (1 knot = 1.15 mi/h)? What is the minimum uncertainty in its position?

5. Calculate the mass of a particle if it is traveling at 2.2×10^6 m/s and has a frequency of 6.67×10^7 Hz. If the uncertainty in the velocity is known to be 0.1%, what is the minimum uncertainty in the position of the particle?

6. Determine the wavelength of a 2800 lb automobile traveling at 80 mi/h ± 3%. How does this compare with the diameter of the nucleus of an atom? You are standing 3 in. from the edge of the highway. What is the minimum uncertainty in the position of the automobile in inches?

Numerical Answers

1. E = 112.3 kJ, ΔT = 0.3893°C, over ten times more light is needed for a 4.0°C increase in temperature

2.

3. 1.7×10^{-35} m, uncertainty in position is ≥ 1.4×10^{-34} m

4.

5. 9.1×10^{-39} kg, uncertainty in position ≥ 2.6 m

6.5: Quantum Mechanics and Atomic Orbitals

Conceptual Problems

1. Why does an electron in an orbital with $n = 1$ in a hydrogen atom have lower energy than a free electron ($n = \infty$)?

2. What four variables are required to fully describe the position of any object in space? In quantum mechanics, one of these variables is not explicitly considered. Which one and why?

3. Chemists generally refer to the square of the wave function rather than to the wave function itself. Why?

4. Orbital energies of species with only one electron are defined by only one quantum number. Which one? In such a species, is the energy of an orbital with $n = 2$ greater than, less than, or equal to the energy of an orbital with $n = 4$? Justify your answer.

5. In each pair of subshells for a hydrogen atom, which has the higher energy? Give the principal and the azimuthal quantum number for each pair.

    1. 1s, 2*p*
    2. 2*p*, 2*s*
    3. 2*s*, 3s
    4. 3*d*, 4s

6. What is the relationship between the energy of an orbital and its average radius? If an electron made a transition from an orbital with an average radius of 846.4 pm to an orbital with an average radius of 476.1 pm, would an emission spectrum or an absorption spectrum be produced? Why?

7. In making a transition from an orbital with a principal quantum number of 4 to an orbital with a principal quantum number of 7, does the electron of a hydrogen atom emit or absorb a photon of energy? What would be the energy of the photon? To what region of the electromagnetic spectrum does this energy correspond?

8. What quantum number defines each of the following?

    1. the overall shape of an orbital
    2. the orientation of an electron with respect to a magnetic field
    3. the orientation of an orbital in space
    4. the average energy and distance of an electron from the nucleus

9. In an attempt to explain the properties of the elements, Niels Bohr initially proposed electronic structures for several elements with orbits holding a certain number of electrons, some of which are in the following table:

Element	Number of Electrons	Electrons in orbits with n =			
		4	3	2	1
H	1				1
He	2				2
Ne	10			8	2
Ar	18		8	8	2
Li	3			1	2
Na	11		1	8	2
K	19	1	8	8	2
Be	4			2	2

    a. Draw the electron configuration of each atom based only on the information given in the table. What are the differences between Bohr's initially proposed structures and those accepted today?

b. Using Bohr's model, what are the implications for the reactivity of each element?
c. Give the actual electron configuration of each element in the table.

Numerical Problems

1. How many subshells are possible for $n = 3$? What are they?
2. How many subshells are possible for $n = 5$? What are they?
3. What value of l corresponds to a d subshell? How many orbitals are in this subshell?
4. What value of l corresponds to an f subshell? How many orbitals are in this subshell?
5. State the number of orbitals and electrons that can occupy each subshell.
    1. 2*s*
    2. 3*p*
    3. 4*d*
    4. 6*f*
6. State the number of orbitals and electrons that can occupy each subshell.
    1. 1s
    2. 4*p*
    3. 5*d*
    4. 4*f*
7. How many orbitals and subshells are found within the principal shell $n = 6$? How do these orbital energies compare with those for $n = 4$?
8. How many nodes would you expect a 4*p* orbital to have? A 5s orbital?
9. A *p* orbital is found to have one node in addition to the nodal plane that bisects the lobes. What would you predict to be the value of *n*? If an *s* orbital has two nodes, what is the value of *n*?

Numerical Answers

1. Three subshells, with $l = 0$ (*s*), $l = 1$ (*p*), and $l = 2$ (*d*).
2.
3. A *d* subshell has $l = 2$ and contains 5 orbitals.
4.
5.
    1. 2 electrons; 1 orbital
    2. 6 electrons; 3 orbitals
    3. 10 electrons; 5 orbitals
    4. 14 electrons; 7 orbitals
6.
7. A principal shell with $n = 6$ contains six subshells, with $l = 0$, 1, 2, 3, 4, and 5, respectively. These subshells contain 1, 3, 5, 7, 9, and 11 orbitals, respectively, for a total of 36 orbitals. The energies of the orbitals with $n = 6$ are higher than those of the corresponding orbitals with the same value of l for $n = 4$.

6.6: Representation of Orbitals

6.7: Many-Electron Atoms

Conceptual Problems

1. A set of four quantum numbers specifies each wave function. What information is given by each quantum number? What does the specified wave function describe?

2. List two pieces of evidence to support the statement that electrons have a spin.

3. The periodic table is divided into blocks. Identify each block and explain the principle behind the divisions. Which quantum number distinguishes the horizontal rows?

4. Identify the element with each ground state electron configuration.

    1. $[He]2s^2 2p^3$
    2. $[Ar]4s^2 3d^1$
    3. $[Kr]5s^2 4d^{10} 5p^3$
    4. $[Xe]6s^2 4f^6$

5. Identify the element with each ground state electron configuration.

    1. $[He]2s^2 2p^1$
    2. $[Ar]4s^2 3d^8$
    3. $[Kr]5s^2 4d^{10} 5p^4$
    4. $[Xe]6s^2$

6. Propose an explanation as to why the noble gases are inert.

Numerical Problems

1. How many magnetic quantum numbers are possible for a 4*p* subshell? A 3*d* subshell? How many orbitals are in these subshells?

2. How many magnetic quantum numbers are possible for a 6s subshell? A 4*f* subshell? How many orbitals does each subshell contain?

3. If $l = 2$ and $m_l = 2$, give all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in the corresponding 3*d* subshell.

4. Give all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 4*d* subshell. How many electrons can the 4*d* orbital accommodate? How would this differ from a situation in which there were only three quantum numbers (n, l, m)?

5. Given the following sets of quantum numbers (n, l, m_l, m_s), identify each principal shell and subshell.

    1. 1, 0, 0, ½
    2. 2, 1, 0, ½
    3. 3, 2, 0, ½
    4. 4, 3, 3, ½

6. Is each set of quantum numbers allowed? Explain your answers.

    1. $n = 2$; $l = 1$; $m_l = 2$; $m_s = +½$
    2. $n = 3$, $l = 0$; $m_l = –1$; $m_s = –½$
    3. $n = 2$; $l = 2$; $m_l = 1$; $m_s = +½$

4. $n = 3$; $l = 2$; $m_l = 2$; $m_s = +½$

7. List the set of quantum numbers for each electron in the valence shell of each element.

    1. beryllium
    2. xenon
    3. lithium
    4. fluorine

8. List the set of quantum numbers for each electron in the valence shell of each element.

    1. carbon
    2. magnesium
    3. bromine
    4. sulfur

9. Sketch the shape of the periodic table if there were three possible values of m_s for each electron (+½, −½, and 0); assume that the Pauli principle is still valid.

10. Predict the shape of the periodic table if eight electrons could occupy the *p* subshell.

11. If the electron could only have spin +½, what would the periodic table look like?

12. If three electrons could occupy each s orbital, what would be the electron configuration of each species?

    1. sodium
    2. titanium
    3. fluorine
    4. calcium

13. If Hund's rule were not followed and maximum pairing occurred, how many unpaired electrons would each species have? How do these numbers compare with the number found using Hund's rule?

    1. phosphorus
    2. iodine
    3. manganese

14. Write the electron configuration for each element in the ground state.

    1. aluminum
    2. calcium
    3. sulfur
    4. tin
    5. nickel
    6. tungsten
    7. neodymium
    8. americium

15. Write the electron configuration for each element in the ground state.

    1. boron
    2. rubidium
    3. bromine
    4. germanium
    5. vanadium
    6. palladium
    7. bismuth
    8. europium

16. Give the complete electron configuration for each element.

1. magnesium
2. potassium
3. titanium
4. selenium
5. iodine
6. uranium
7. germanium

17. Give the complete electron configuration for each element.

    1. tin
    2. copper
    3. fluorine
    4. hydrogen
    5. thorium
    6. yttrium
    7. bismuth

18. Write the valence electron configuration for each element:

    1. samarium
    2. praseodymium
    3. boron
    4. cobalt

19. Using the Pauli exclusion principle and Hund's rule, draw valence orbital diagrams for each element.

    1. barium
    2. neodymium
    3. iodine

20. Using the Pauli exclusion principle and Hund's rule, draw valence orbital diagrams for each element.

    1. chlorine
    2. silicon
    3. scandium

21. How many unpaired electrons does each species contain?

    1. lead
    2. cesium
    3. copper
    4. silicon
    5. selenium

22. How many unpaired electrons does each species contain?

    1. helium
    2. oxygen
    3. bismuth
    4. silver
    5. boron

23. For each element, give the complete electron configuration, draw the valence electron configuration, and give the number of unpaired electrons present.

    1. lithium
    2. magnesium
    3. silicon
    4. cesium

5. lead

24. Use an orbital diagram to illustrate the aufbau principle, the Pauli exclusion principle, and Hund's rule for each element.

    1. carbon
    2. sulfur

Numerical Answers

1. For a 4*p* subshell, $n = 4$ and $l = 1$. The allowed values of the magnetic quantum number, m_l, are therefore +1, 0, –1, corresponding to three 4*p* orbitals. For a 3*d* subshell, $n = 3$ and $l = 2$. The allowed values of the magnetic quantum number, m_l, are therefore +2, +1, 0, –1, –2, corresponding to five 3*d* orbitals.

6.8: Electron Configurations

6.9: Electron Configurations and the Periodic Table

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6.S: Electronic Structure of Atoms (Summary)

Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A basic knowledge of the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A wave is a periodic oscillation by which energy is transmitted through space. All waves are periodic, repeating regularly in both space and time. Waves are characterized by several interrelated properties.

- **Electronic structure**: arrangement of electrons in atoms
- **Electromagnetic radiation**: aka **radiant energy**; form of energy that has wave characteristics and carries energy through space. *All types of electromagnetic radiation move through a vacuum at a speed of 3.00 X 10^8 m/s (speed of light).*
- **Wavelength**: the distance between identical points on successive waves
- **Frequency**: the number of complete wavelengths that pass a given point in 1s

$$\nu\lambda = c$$

where ν = frequency, λ= wavelength, and c = speed of light

Wavelength is expressed in units of length.

- **Electromagnetic spectrum**: various types of electromagnetic radiations arranged in order of increasing wavelength.

Frequency is expressed in Hertz (Hz), also denoted by s^{-1} or /s

Quantum Effects and Photons

- **Quantum**: smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation

$$E = hv$$

where E = energy, h = Planck's constant, ν = frequency

Planck's constant = 6.63 X 10^{-34} J•s

According to Planck's theory, energy is always emitted or absorbed in whole-number multiples of *hv*, for example, *hv*, *2hv*, *3hv*, and so forth. We say that the allowed energies are *quantized* (that is, their values are restricted to certain quantities).

6.2: Quantized Energy and Photons

Blackbody radiation is the radiation emitted by hot objects and could not be explained with classical physics. Max Planck postulated that energy was quantized and may be emitted or absorbed only in integral multiples of a small unit of energy, known as a quantum. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant h is a fundamental constant (Planck's constant). Albert Einstein used the quantization of energy to explain the photoelectric effect

- The photoelectric effect: when photons of sufficiently high energy strike a metal surface, electrons are emitted from the metal. The emitted electrons are drawn toward the other electrode, which is a positive terminal. As a result, current flows in a circuit.
- **Photon***:* smallest increment (a *quantum*) of radiant energy; a photon of light with frequency v has an energy equal to *hv*.
- When a photon strikes the metal, its energy is transferred to an electron in the metal. A certain amount of energy is required for the electron to overcome the attractive forces that hold it within the metal. If the photons have less energy that this energy threshold, the electrons cannot escape from the metal surface. If a photon has sufficient energy, an electron is emitted. If the photon has more energy than necessary, the excess appears as kinetic energy of the emitted electron.

6.3: Line Spectra and the Bohr Model

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Most light is

polychromatic and contains light of many wavelengths. Light that has only a single wavelength is monochromatic and is produced by devices called lasers, which use transitions between two atomic energy levels to produce light in a very narrow range of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy e

Line Spectra

Radiation composed of a single wavelength is said to be *monochromatic*.

- **Spectrum**: distribution among various wavelengths of the radiant energy emitted or absorbed by an object
- **Continuous spectrum**: rainbow of colors, containing light of all wavelengths. *Not all radiation sources produce a continuous spectrum*
- **Line spectrum**: spectrum containing radiation of only specific wavelengths

Bohr's Model

Electrons in a permitted orbit have a specific energy and are said to be in an "allowed" energy state. An electron in an allowed energy state will not radiate energy and therefore will not spiral into the nucleus.

$$E_n = -R_H \frac{1}{n^2}$$

- R_H = Rydberg constant: 2.18 X 10^{-18} J
- n = principal quantum number, corresponds to the different allowed orbits for the electron

All energies given by this equation will be negative. The lower (more negative) the energy is, the more stable the atom is. The lowest energy state is that for which n=1.

- **Ground state:** lowest energy state of an atom, n=1
- **Excited state:** when the electron is in higher energy orbit (less negative), n=2 or higher

If n becomes infinitely large (∞), the electron is completely separated from the nucleus:

$$E_\infty = (-2.18 \times 10^{-18} J)\left(\frac{1}{\infty^2}\right) = 0$$

Thus, the state in which the electron is removed from the nucleus is the reference, or zero-energy, state of the hydrogen atom. It is important to remember that this zero-energy state is higher in energy than the states with negative energies

Electrons can change from one energy state to another by absorbing or emitting radiant energy. Radiant energy must be absorbed for an electron to move to a higher energy state, but is emitted when the electron moves to a lower energy state. .

$$\Delta E = E_f - E_i$$

- If $n_f > n_i$, then ΔE is positive, radiant energy is absorbed
- If $n_f < n_i$, then ΔE is negative, radiant energy is emitted

6.4: The Wave Behavior of Matter

An electron possesses both particle and wave properties. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle. The electron in Bohr's circular orbits could thus be described as a standing wave, one that does not move through space. Werner Heisenberg's uncertainty principle states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

- **Momentum**: the product of the mass, *m*, and the velocity, *v*, of a particle
- **Matter waves**: term used to describe the wave characteristics of a particle

$$\lambda = h/mv$$

λ = wavelength, h = Planck's constant, m = mass, v = velocity

The Uncertainty Principle

- **Uncertainty principle**: theory first put forth by Heisenberg, states that is it impossible to determine both the exact momentum of the electron and its exact location.

6.5: Quantum Mechanics and Atomic Orbitals

There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of quantum mechanics, which uses wavefunctions to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies.

- **Wave functions**: represented by ψ, square of wave function, ψ^2, provides information about an electron's location when it is in an allowed energy state.
- **Probability density**: represented by ψ^2, value that represents the probability that an electron will be found at a given point in space
- **Electron density**: the probability of finding and electron at any particular point in an atom. Equals ψ^2.

Orbitals and Quantum Numbers

-**Orbital**: allowed energy state of an electron in the quantum-mechanical model of the atom; also used to describe the spatial distribution of an electron. Defined by the value of 3 quantum numbers; *n, l, and* m_l.

value of 3 quantum numbers; n, l, and ml.

Value of l	0	1	2	3
Letter used	s	p	d	f

1. The principal quantum number, *n*, can have integral values of 1, 2, 3 and so forth. As *n* increases, the orbital becomes larger; the electron has a higher energy and is farther away from the nucleus.
2. The second quantum number, *l*, can have integral values from 0 to *n* − 1 for each value of *n*. This quantum number defines the shape of the orbital. Generally designated by the letters s, *p*, *d*, and *f*. These correspond to values ranging from 0 to 3.
3. The magnetic quantum number, m_l, can have integral values between *l* and –*l*, including zero. This quantum number describes the orientation of the orbital in space.

Electron shell: collection of orbitals with the same value of *n*

Subshell: one or more orbitals with the same set of *n* and *l* values

1. Each shell is divided into the number of subshells equal to the principal quantum number, *n*, for that shell. The first shell consists of only the 1s subshell; the second shell consists of two subshells, 2s and 2p; the third of three subshell, 3s, 3p and 3d, and so forth.
2. Each subshell is divided into orbitals. Each s subshell consists of one orbital; each *p* subshell of three orbitals, each *d* subshell of five, and each *f* subshell of seven orbitals.

6.6: 3D Representation of Orbitals

Orbitals with l = 0 are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. Orbitals with values of n > 1 and l = 0 contain one or more nodes. Orbitals with l = 1 are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with l = 2 are d orbitals and have more complex shapes with at least two nodal surfaces. l = 3 orbitals are f orbitals, which are still more complex.

The s Orbitals: 1s orbital: most stable, spherically symmetric, figure indicates that the probability decreases as we move away from the nucleus. ALL s ORBITALS ARE SPHERICALLY SYMMETRIC.

- **Nodal surfaces (nodes)**: intermediate regions where ψ^2 goes to zero. The number of nodes increases with increasing value

for the principal quantum number, *n*.

The *p* Orbitals: Electron density is concentrated on two sides of the nucleus, separated by a node at the nucleus. The orbitals of a given subshell have the same size and shape but differ from each other in orientation. The axis along which the orbital is oriented is not related to m_l.

6.7: Many-Electron Atoms

In addition to the three quantum numbers (n, l, ml) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the electron spin quantum number (ms), which can have values of +½ or –½ for any electron, corresponding to the two possible orientations of an electron in a magnetic field. This is important for chemistry because the Pauli exclusion principle implies that no orbital can contain more than two electrons (with opposite spin).

Although the shapes of the orbitals for many-electron atoms are the same as those for hydrogen, the presence of more than one electron greatly changes the energies of the orbitals. In hydrogen, the energy of an orbital depends only on its principal quantum number, however, in many-electron atoms, electron-electron repulsions cause different subshells to be at different energies

Effective Nuclear Charge

- *Effective nuclear charge*: net positive charge attracting electrons

$$Z_{eff} = Z–S$$

- Z_{eff} = effective nuclear charge
- Z = number of protons in the nucleus
- S = average number of electrons between the nucleus and electron in question

- *Screening effect*: effect of inner electrons in decreasing the nuclear charge experienced by outer electrons

Energies of Orbitals

The extent to which an electron will be screened by the other electrons depends on its electron distribution as we move outward from the nucleus.

- *In a many-electron atom, for a given value of n, Z_{eff} decreases with increasing value of l.*
- *In a many-electron atom, for a given value of n, the energy of an orbital increases with increasing value of l.*

Degenerate: orbitals that have the same energy

Electron Spin and the Pauli Exclusion Principle

- **Electron spin**: property of the electron that makes it behave as though it were a tiny magnet. The electron behaves as if it were spinning on its axis; electron spin is quantized.
- **Electron spin quantum number**: denoted as m_s. It can only have two possible values, +½ and –½, which we can interpret as indicating the two opposite directions in which the electron can spin.
- **Pauli exclusion principle**: states that no two electrons in an atom can have the same set of four quantum numbers *n*, *l*, m_l, m_s. This means that if we wish to put two electrons in an orbital and satisfy Pauli's exclusion principle, our only choice is to assign different m_s values to the electrons. Because there are only two values, *we can conclude that an electron can hold a maximum of two electrons and they must have opposite spins.*

6.8: Electron Configurations

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the aufbau principle), which gives rise to a particular arrangement of electrons for each element (its electron configuration). Hund's rule says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with parallel spins.

- **Electron configuration**: the way in which the electrons are distributed among the various orbitals. The most stable, or

ground, electron configuration of an atom is that in which the electrons are in the lowest possible energy level
- **Orbital diagram**: representation of electron configuration in which each orbital is represented by a box and each electron by a half-arrow. A half-arrow pointing upward represents an electron with positive spin; one pointing downward represents an electron with a negative spin.

Writing Electron Configurations

- **Hund's rule**: rule stating that electrons occupy degenerate orbitals in such a way as to maximize the number of electrons with the same spin. In other words, each orbital has one electron placed in it before paring of electron in orbitals occurs. Note that this rule applies to orbitals that are *degenerate*, which means that they have the same energy.
- **Valence electrons**: electrons in the outer shells
- **Core electrons**: electrons in the inner shells
- **Transition elements**: aka **Transition metals**; elements of the *d* orbitals
- **Lanthanide elements**: aka **Rare-earth elements**; 14 elements of the 4f orbitals, # 58-71
- **Actinide elements**: 14 elements of 5f orbitals, # 90-103. Most are not found in nature.

6.9: Electron Configurations and the Periodic Table

The arrangement of atoms in the periodic table results in blocks corresponding to filling of the ns, np, nd, and nf orbitals to produce the distinctive chemical properties of the elements in the s block, p block, d block, and f block, respectively.

- **Main group elements**: aka **Representatives**; *s* and *p* block elements
- **F-block metals**: 28 elements located below the table, *f* block elements

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7: PERIODIC PROPERTIES OF THE ELEMENTS

Last chapter, we presented the contemporary quantum mechanical model of the atom. In using this model to describe the electronic structures of the elements in order of increasing atomic number, we saw that periodic similarities in electron configuration correlate with periodic similarities in properties, which is the basis for the structure of the periodic table. For example, the noble gases have what is often called filled or closed-shell valence electron configurations. These closed shells are actually filled *s* and *p* subshells with a total of eight electrons, which are called *octets*; helium is an exception, with a closed 1s shell that has only two electrons. Because of their filled valence shells, the noble gases are generally unreactive. In contrast, the alkali metals have a single valence electron outside a closed shell and readily lose this electron to elements that require electrons to achieve an octet, such as the halogens. Thus because of their periodic similarities in electron configuration, atoms in the same column of the periodic table tend to form compounds with the same oxidation states and stoichiometries. Last chapter ended with the observation that, because all the elements in a column have the same valence electron configuration, the periodic table can be used to find the electron configuration of most of the elements at a glance.

In this chapter, we explore the relationship between the electron configurations of the elements, as reflected in their arrangement in the periodic table, and their physical and chemical properties. In particular, we focus on the similarities between elements in the same column and on the trends in properties that are observed across horizontal rows or down vertical columns. By the end of this chapter, your understanding of these trends and relationships will provide you with clues as to why argon is used in incandescent light bulbs, why coal and wood burst into flames when they come in contact with pure F_2, why aluminum was discovered so late despite being the third most abundant element in Earth's crust, and why lithium is commonly used in batteries. We begin by expanding on the brief discussion of the history of the periodic table and describing how it was created many years before electrons had even been discovered, much less discussed in terms of shells, subshells, orbitals, and electron spin.

7.1: Development of the Periodic Table

7.2: Shielding and Effective Nuclear Charge

7.3: Sizes of Atoms and Ions

7.4: Ionization Energy

7.5: Electron Affinities

7.6: Metals, Nonmetals, and Metalloids

7.7: Group Trends for the Active Metals

7.8: Group Trends for Selected Nonmetals

7.E: Periodic Properties of the Elements (Exercises)

7.S: Periodic Properties of the Elements (Summary)

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7.1: Development of the Periodic Table

Learning Objectives

- To become familiar with the history of the periodic table.

The modern periodic table has evolved through a long history of attempts by chemists to arrange the elements according to their properties as an aid in predicting chemical behavior. One of the first to suggest such an arrangement was the German chemist Johannes Dobereiner (1780–1849), who noticed that many of the known elements could be grouped in triads (a set of three elements that have similar properties)—for example, chlorine, bromine, and iodine; or copper, silver, and gold. Dobereiner proposed that all elements could be grouped in such triads, but subsequent attempts to expand his concept were unsuccessful. We now know that portions of the periodic table—the *d* block in particular—contain triads of elements with substantial similarities. The middle three members of most of the other columns, such as sulfur, selenium, and tellurium in group 16 or aluminum, gallium, and indium in Group 13, also have remarkably similar chemistry.

No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co & Ni 22	Br 29	Pd 36	I 42	Pt & Ir 50
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Tl 51
G 3	Mg 10	Ca 17	Zn 25	Sr 31	Bd [sic-Cd] 38	Ba & V 45	Pb 54
Bo 4	Al 11	Cr 19	Y 24	Ce & La 33	U 40	Ta 46	Th 56
C 5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Hg 52
N 6	**P 13**	Mn 20	**As 27**	Di & Mo 34	**Sb 41**	Nb 48	**Bi 55**
O 7	S 14	Fe 21	Se 28	Ro & Ru 35	Te 43	Au 49	Os 51

NOTE. Where two elements happen to have the same equivalent, both are designated by the same number.

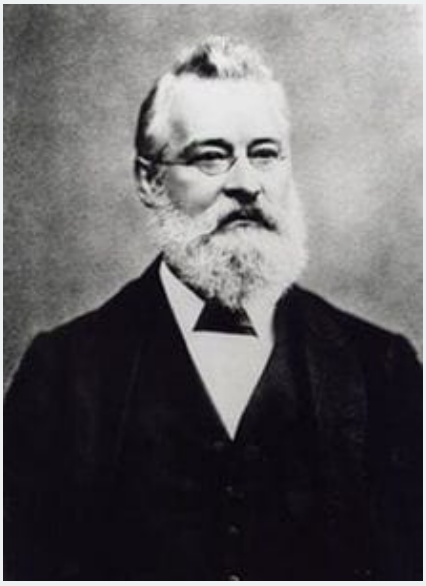
Figure 7.1.1: The Arrangement of the Elements into Octaves as Proposed by Newlands. The table shown here accompanied a letter from a 27-year-old Newlands to the editor of the journal *Chemical News* in which he wrote: "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also. This peculiar relationship I propose to provisionally term the *Law of Octaves*. I am, &c. John A. R. Newlands, F.C.S. Laboratory, 19, Great St. Helen's, E.C., August 8, 1865."

By the mid-19th century, the atomic masses of many of the elements had been determined. The English chemist John Newlands (1838–1898), hypothesizing that the chemistry of the elements might be related to their masses, arranged the known elements in order of increasing atomic mass and discovered that every seventh element had similar properties (Figure 7.1.1). Newlands therefore suggested that the elements could be classified into octaves. He described octaves as a group of seven elements which correspond to the horizontal rows in the main groups of today's periodic table. There were seven elements because the noble gases were not known at the time. Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed. At one scientific meeting, Newlands was asked why he didn't arrange the elements in alphabetical order instead of by atomic mass, since that would make just as much sense! Actually, Newlands was on the right track—with only a few exceptions, atomic mass does increase with atomic number, and similar properties occur every time a set of ns^2np^6 subshells is filled. Despite the fact that Newlands's table had no logical place for the *d*-block elements, he was honored

for his idea by the Royal Society of London in 1887.

John Newlands (1838–1898)

John Alexander Reina Newlands was an English chemist who worked on the development of the periodic table. He noticed that elemental properties repeated every seventh (or multiple of seven) element, as musical notes repeat every eighth note.



The periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830–1895) and the Russian chemist Dimitri Mendeleev (1834–1907), both of whom focused on the relationships between atomic mass and various physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the elements in his table according to periodic variations in simple atomic properties, such as “atomic volume” (Figure 7.1.2), which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density (ρ) of the element in grams per cubic centimeter. This property is equivalent to what is today defined as molar volume, the molar mass of an element divided by its density, (measured in cubic centimeters per mole):

$$\frac{molar\ mass\ \left(\not{g}/mol\right)}{density\ \left(\not{g}/cm^3\right)} = molar\ volume\ \left(cm^3/mol\right) \tag{7.1.1}$$

As shown in Figure 7.1.2, the alkali metals have the highest molar volumes of the solid elements. In Meyer’s plot of atomic volume versus atomic mass, the nonmetals occur on the rising portion of the graph, and metals occur at the peaks, in the valleys, and on the downslopes.

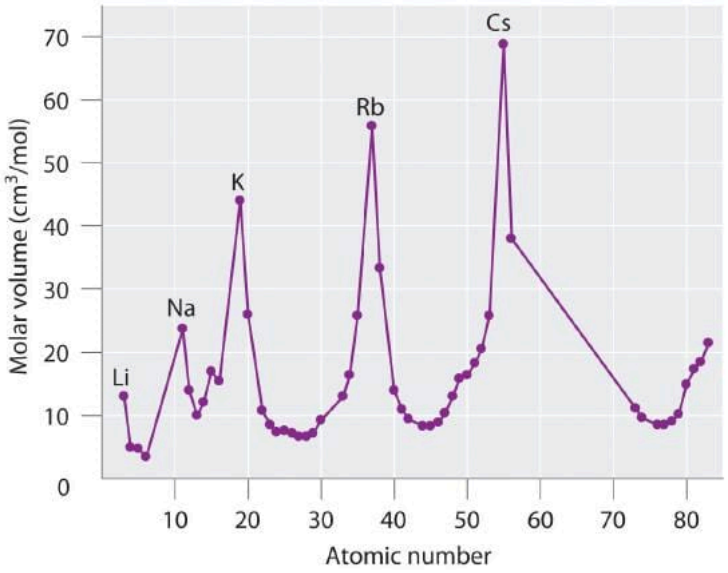
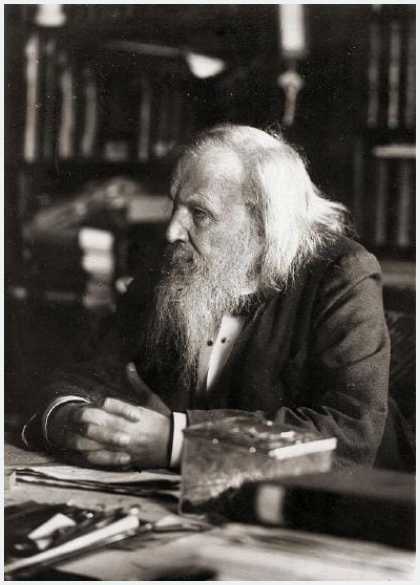


Figure 7.1.2: Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of 1870. Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (Group 1).

Dimitri Mendeleev (1834–1907)

When his family's glass factory was destroyed by fire, Mendeleev moved to St. Petersburg, Russia, to study science. He became ill and was not expected to recover, but he finished his PhD with the help of his professors and fellow students.



In addition to the periodic table, another of Mendeleev's contributions to science was an outstanding textbook, *The Principles of Chemistry*, which was used for many years.

Mendeleev's Periodic Table

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7.2: Shielding and Effective Nuclear Charge

Learning Objectives

- To understand the basics of electron shielding and penetration

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies. These effects are the underlying basis for the periodic trends in elemental properties that we will explore in this chapter.

Electron Shielding and Effective Nuclear Charge

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, many of the other electrons will be *between* that electron and the nucleus (Figure $7.2.1$). Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is less than the actual nuclear charge Z. This effect is called **electron shielding**.

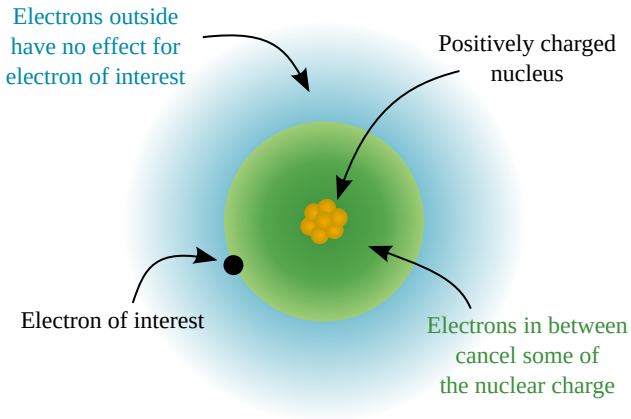


Figure $7.2.1$: This image shows how inner electrons can shield outer electrons from the nuclear charge. (CC BY-SA 3.0; NikNaks via Wikipedia).

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other ($Z-1$) electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z:

$$1 \leq Z_{eff} \leq Z.$$

Notice that $Z_{eff} = Z$ only for hydrogen (Figure 7.2.2).

Definition: Shielding

Shielding refers to the core electrons repelling the outer electrons, which lowers the effective charge of the nucleus on the outer electrons. Hence, the nucleus has "less grip" on the outer electrons insofar as it is shielded from them.

Z_{eff} can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation:

$$Z_{eff} = Z - S \tag{7.2.1}$$

where Z is the atomic number (number of protons in nucleus) and S is the shielding constant and is approximated by number of electrons between the nucleus and the electron in question (*the number of nonvalence electrons*). The value of Z_{eff} will provide information on how much of a charge an electron actually experiences.

We can see from Equation 7.2.1 that the effective nuclear charge of an atom increases as the number of protons in an atom increases (Figure 7.2.2). As we will discuss later on in the chapter, this phenomenon can explain the decrease in atomic radii we see as we go across the periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge.

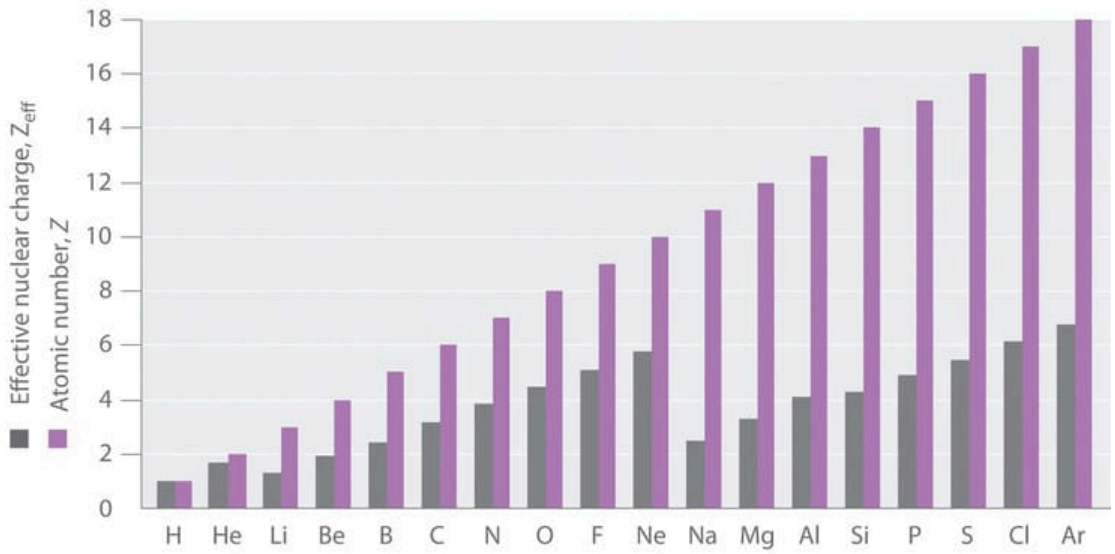


Figure 7.2.2: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the (CC BY-SA-NC 3.0; anonynous)

The shielding constant can be estimated by totaling the screening by **all nonvalence electrons** (n) except the one in question.

$$S = \sum_{i}^{n-1} S_i \tag{7.2.2}$$

where S_i is the shielding of the ith electron.

> Electrons that are shielded from the full charge of the nucleus experience an *effective nuclear charge* (Z_{eff}) of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogenlike ion.

From Equations 7.2.1 and 7.2.2, Z_{eff} for a specific electron can be estimated is the shielding constants for that electron of all other electrons in species is known. A simple approximation is that all other non-valence electrons shield equally and fully:

$$S_i = 1 \tag{7.2.3}$$

This crude approximation is demonstrated in Example 7.2.1.

Example 7.2.1: Fluorine, Neon, and Sodium

What is the effective attraction Z_{eff} experienced by the valence electrons in the three isoelectronic species: the fluorine anion, the neutral neon atom, and sodium cation?

Solution

Each species has 10 electrons, and the number of nonvalence electrons is 2 (10 total electrons - 8 valence), but the effective nuclear charge varies because each has a different atomic number A. This is an application of Equations 7.2.1 and 7.2.2. We use the simple assumption that all electrons shield equally and fully the valence electrons (Equation 7.2.3).

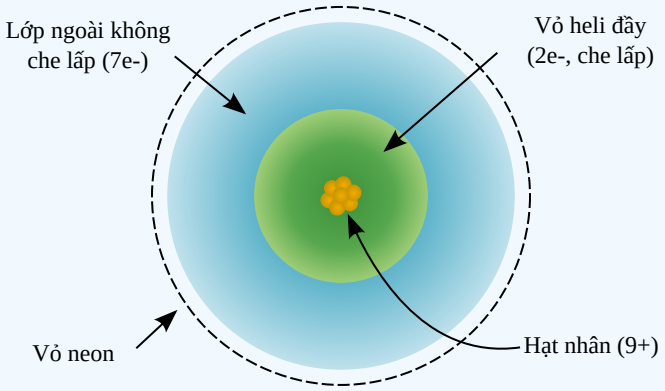


Diagram of a fluorine atom showing the extent of effective nuclear charge. (CC BY-SA 3.0; NikNaks via Wikipedia).

The charge Z of the nucleus of a fluorine atom is 9, but the valence electrons are screened appreciably by the core electrons (four electrons from the 1s and 2s orbitals) and partially by the 7 electrons in the 2p orbitals.

- $Z_{\text{eff}}(\text{F}^-) = 9 - 2 = 7+$
- $Z_{\text{eff}}(\text{Ne}) = 10 - 2 = 8+$
- $Z_{\text{eff}}(\text{Na}^+) = 11 - 2 = 9+$

So the sodium cation has the greatest effective nuclear charge. This also suggests that Na^+ has the smallest radius of these species and that is correct.

Exercise 7.2.1: Magnesium Species

What is the effective attraction Z_{eff} experienced by the valence electrons in the magnesium anion, the neutral magnesium atom, and magnesium cation? Use the simple approximation for shielding constants. Compare your result for the magnesium atom to the more accurate value in Figure 7.2.2 and proposed an origin for the difference.

Answer available at the end of this section.

Electron Penetration

The approximation in Equation 7.2.3 is a good first order description of electron shielding, but the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 7.2.2 for the elements of the first three rows of the periodic table.

Penetration describes the proximity to which an electron can approach to the nucleus. In a multi-electron system, electron penetration is defined by an electron's relative electron density (probability density) near the nucleus of an atom (Figure 7.2.3).

Electrons in different orbitals have different electron densities around the nucleus. In other words, penetration depends on the shell (n) and subshell (l).

For example, a 1s electron (Figure 7.2.3; purple curve) has greater electron density near the nucleus than a 2p electron (Figure 7.2.3 ; red curve) and has a greater penetration. This related to the shielding constants since the 1s electrons are closer to the nucleus than a 2p electron, hence the 1s screens a 2p electron almost perfectly ($S = 1$. However, the 2s electron has a lower shielding constant ($S < 1$ because it can penetrate close to the nucleus in the small area of electron density within the first spherical node (Figure 7.2.3; green curve). In this way the 2s electron can "avoid" some of the shielding effect of the inner 1s electron.

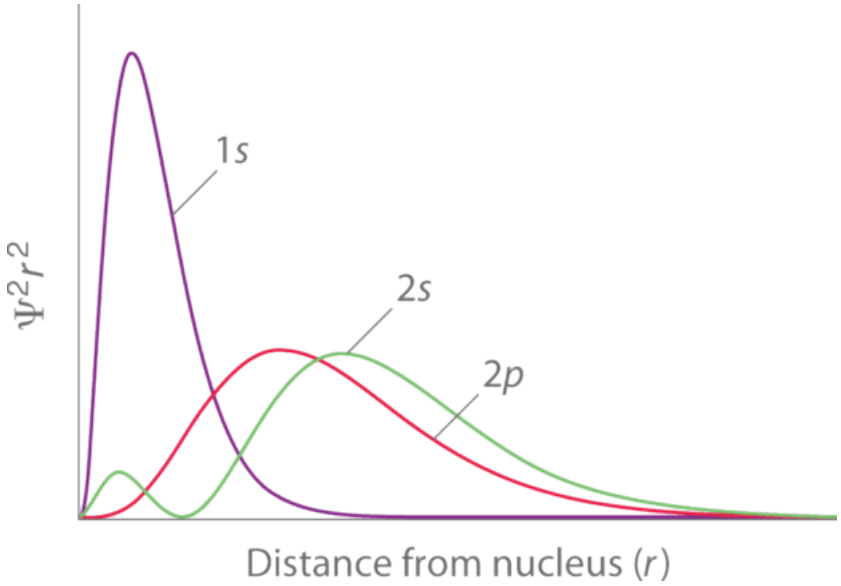


Figure 7.2.3: Orbital Penetration. A comparison of the radial probability distribution of the 2*s* and 2*p* orbitals for various states of the hydrogen atom shows that the 2*s* orbital penetrates inside the 1*s* orbital more than the 2*p* orbital does. Consequently, when an electron is in the small inner lobe of the 2*s* orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital. (CC BY-NC-SA 3.0; Anonymous)

For the same shell value (n) the penetrating power of an electron follows this trend in subshells (Figure 7.2.3):

$$s > p > d \approx f. \tag{7.2.4}$$

for different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:

$$1\text{s} > 2\text{s} > 2\text{p} > 3\text{s} > 3\text{p} > 4\text{s} > 3\text{d} > 4\text{p} > 5\text{s} > 4\text{d} > 5\text{p} > 6\text{s} > 4\text{f} \ \ldots \tag{7.2.5}$$

Definition: Penetration

Penetration describes the proximity of electrons in an orbital to the nucleus. Electrons that have greater penetration can get closer to the nucleus and effectively block out the charge from electrons that have less proximity.

Table 7.2.1: Effective Nuclear Charges for Selected Atoms

Atom	Sublevel	Z	Z_{eff}
H	1s	1	1
He	1s	2	1.69
Li	1s, 2s	3	2.69, 1.28
Be	1s, 2s	4	3.68, 1.91
B	1s, 2s, 2p	5	4.68, 2.58, 2.42
F	1s, 2s, 2p	9	8.65, 5.13, 5.10

Atom	Sublevel	Z	Z_{eff}
Na	1s, 2s, 2p, 3s	11	10.63, 6.57, 6.80, 2.51

Data from E. Clementi and D. L. Raimondi; The Journal of Chemical Physics 38, 2686 (1963).

Because of the effects of shielding and the different radial distributions of orbitals with the same value of *n* but different values of *l*, the different subshells are not degenerate in a multielectron atom. For a given value of *n*, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of *n*; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

A Better Estimation of Shielding: Slater Rules

The concepts of electron shielding, orbital penetration and effective nuclear charge were introduced above, but we did so in a qualitative manner (e.g., Equations 7.2.4 and 7.2.5). A more accurate model for estimating electron shielding and corresponding effective nuclear charge experienced is Slater's Rules. However, the application of these rules is outside the scope of this text.

YouTube Video

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Zeff and Electron Shielding: Zeff and Electron Shielding(opens in new window) [youtu.be]

Summary

The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge** (Z_{eff}) to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of *l* and the same value of *n* overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

Answers

Exercise 7.2.1**: Magnesium Species**

- $Z_{\text{eff}}(\text{Mg}^{-}) = 12 - 10 = 2+$
- $Z_{\text{eff}}(\text{Mg}) = 12 - 10 = 2+$
- $Z_{\text{eff}}(\text{Mg}^{+}) = 12 - 10 = 2+$

Remember that the simple approximations in Equations 7.2.2 and 7.2.3 suggest that valence electrons **do not shield** other valence electrons. Therefore, each of these species has the same number of non-valence electrons and Equation 7.2.1 suggests the effective charge on each valence electron is identical for each of the three species.

This is not correct and a more complex model is needed to predict the experimental observed Z_{eff} value. The ability of valence electrons to shield other valence electrons or in partial amounts (e.g., $S_i \neq 1$) is in violation of Equations 7.2.2 and 7.2.3. That fact that these approximations are poor is suggested by the experimental Z_{eff} value shown in Figure 7.2.2 for Mg of 3.2+. This is appreciably larger than the +2 estimated above, which means these simple approximations overestimate the total shielding constant S. A more sophisticated model is needed.

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7.3: Sizes of Atoms and Ions

Learning Objectives

- To understand periodic trends in atomic radii.
- To predict relative ionic sizes within an isoelectronic series.

Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes; however, some atoms are larger or smaller than others, and this influences their chemistry. In this section, we discuss how atomic and ion "sizes" are defined and obtained.

Atomic Radii

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure 7.3.1 which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

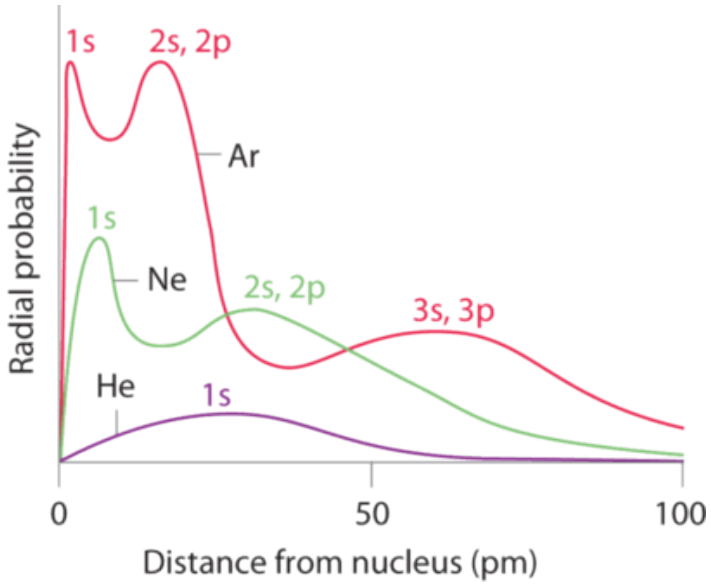


Figure 7.3.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1s electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈8 pm, and the 2s and 2p electrons combine to form another maximum at ≈35 pm (the n = 2 shell). In Ar, the 1s electrons have a maximum at ≈2 pm, the 2s and 2p electrons combine to form a maximum at ≈18 pm, and the 3s and 3p electrons combine to form a maximum at ≈70 pm.

Figure 7.3.1 also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell (n = 1), it shows only a single peak. In contrast, neon, with filled n = 1 and 2 principal shells, has two peaks. Argon, with filled n = 1, 2, and 3 principal shells, has three peaks. The peak for the filled n = 1 shell occurs at successively shorter distances for neon (Z = 10) and argon (Z = 18) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n. Consequently, the two electrons in the n = 1 shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the n = 1 shell also decreases tremendously (the filled 1s orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled n = 2 shell in argon is located closer to the nucleus and has a lower energy than the n = 2 shell in neon.

Figure 7.3.1 illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a **covalent atomic radius** (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (Figure 7.3.2*a*). Atomic radii are often measured in angstroms (Å), a non-SI unit: 1 Å = 1×10^{-10} m = 100 pm.

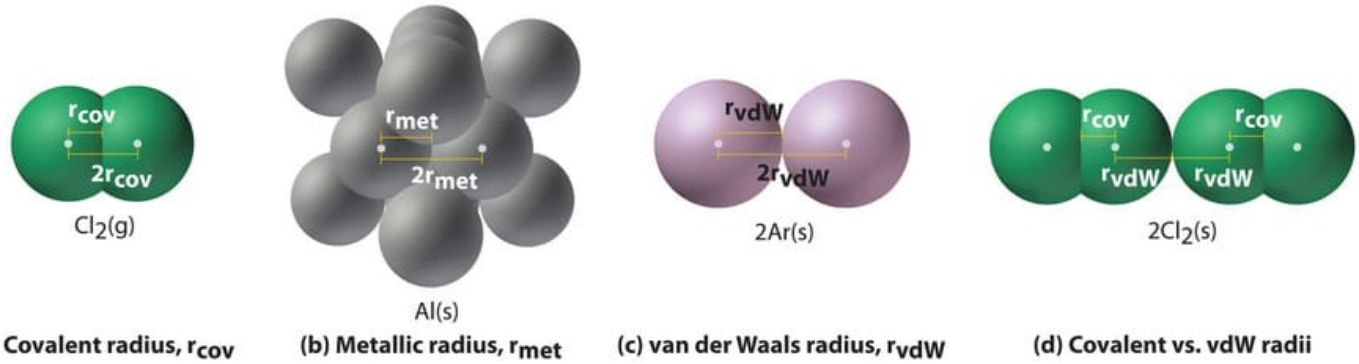


Figure 7.3.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is half the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is half the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?

In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds. A similar approach for measuring the size of ions is discussed later in this section.

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the **metallic atomic radius** (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms in the solid (Figure 7.3.2*b*). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the **van der Waals atomic radius** (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (Figure 7.3.2*c*). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $Cl_2\,(s)$ at low temperatures). These radii are generally not the same (Figure 7.3.2*d*).

Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 7.3.3).

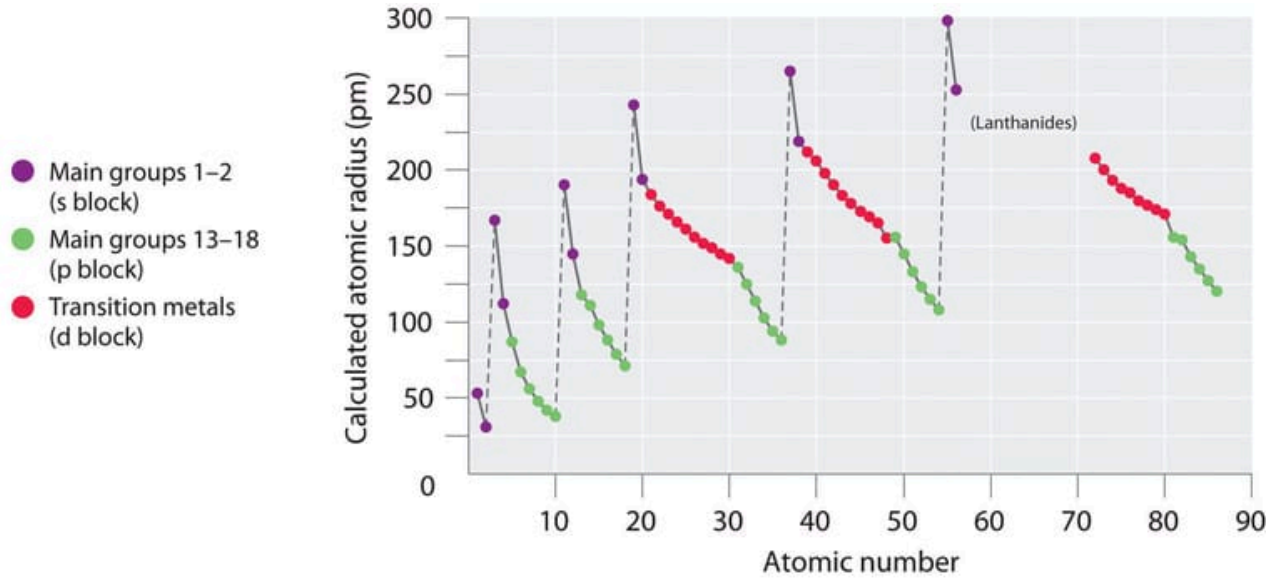


Figure 7.3.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table

In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 7.3.4).

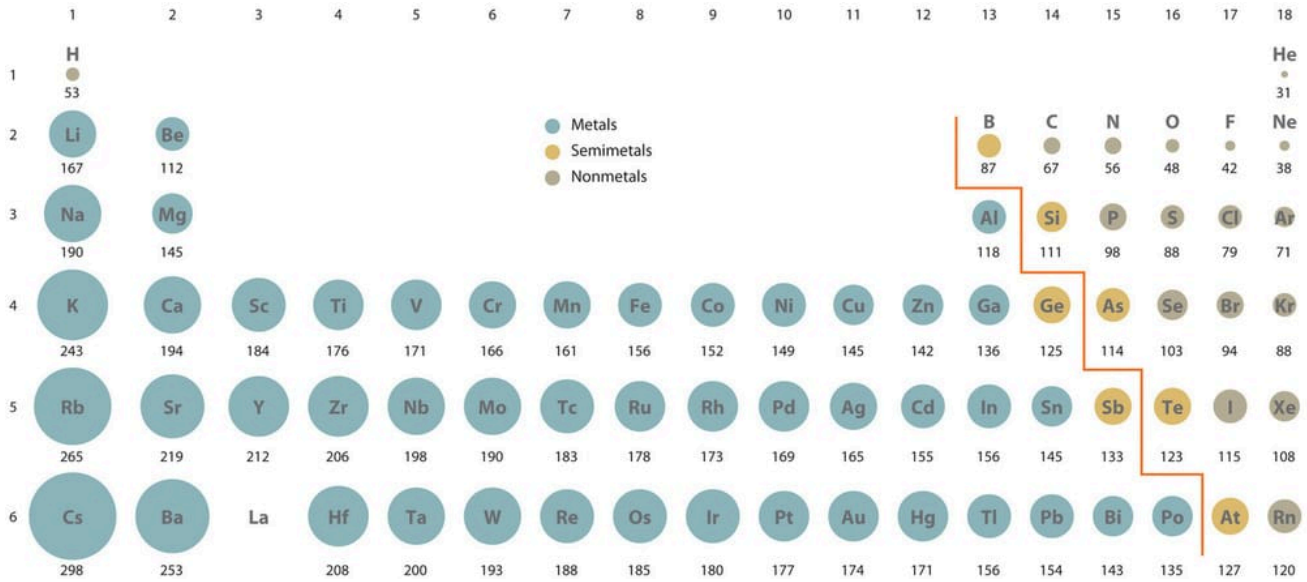


Figure 7.3.4 Calculated Atomic Radii (in Picometers) of the *s*-, *p*-, and *d*-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: Web elements [www.webelements.com]. Web Elements is an excellent online source for looking up atomic properties.

Trends in atomic size result from differences in the **effective nuclear charges** (Z_{eff}) experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always *less* than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

Atomic radii decrease from left to right across a row and increase from top to bottom down a column.

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the 2*s* and 2*p* orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2*s* electron in lithium experiences an effective nuclear charge of approximately +1 because the

electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.) In contrast, the two 2*s* electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2*s* electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2*s* and 2*p* orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size (Figure 7.3.5).

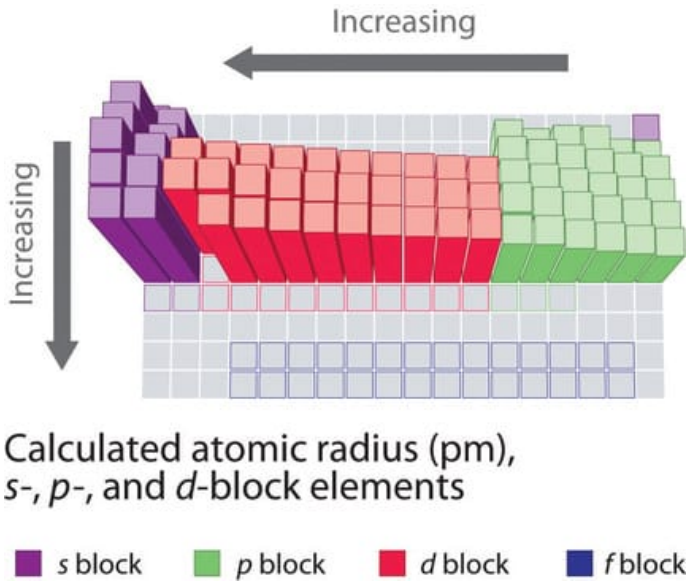


Figure 7.3.5: The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.

The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number *n* is not constant. As we saw in Chapter 2, the size of the orbitals increases as *n* increases, *provided the nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to *ns* orbitals with increasing values of *n*. However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number *n* increases from 2 to 6, but the nuclear charge increases from +3 to +55!

As a consequence the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the the inner electrons. If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration. The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ shells, abbreviated as $[Xe]5s^2 4d^{10} 5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the

other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

Not all Electrons shield equally

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

Example 7.3.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing atomic radius: aluminum, carbon, and silicon.

Given: three elements

Asked for: arrange in order of increasing atomic radius

Strategy:

A. Identify the location of the elements in the periodic table. Determine the relative sizes of elements located in the same column from their principal quantum number *n*. Then determine the order of elements in the same row from their effective nuclear charges. If the elements are not in the same column or row, use pairwise comparisons.
B. List the elements in order of increasing atomic radius.

Solution:

A These elements are not all in the same column or row, so we must use pairwise comparisons. Carbon and silicon are both in group 14 with carbon lying above, so carbon is smaller than silicon (C < Si). Aluminum and silicon are both in the third row with aluminum lying to the left, so silicon is smaller than aluminum (Si < Al) because its effective nuclear charge is greater.

B Combining the two inequalities gives the overall order: C < Si < Al.

Exercise 7.3.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

Answer available at the end of this section.

YouTube Video

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Atomic Radius: Atomic Radius, YouTube(opens in new window) [youtu.be]

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom to form a positive ion (cation) or when additional electrons attach themselves to neutral atoms to form a negative one (anion). The designations cation or anion come

from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

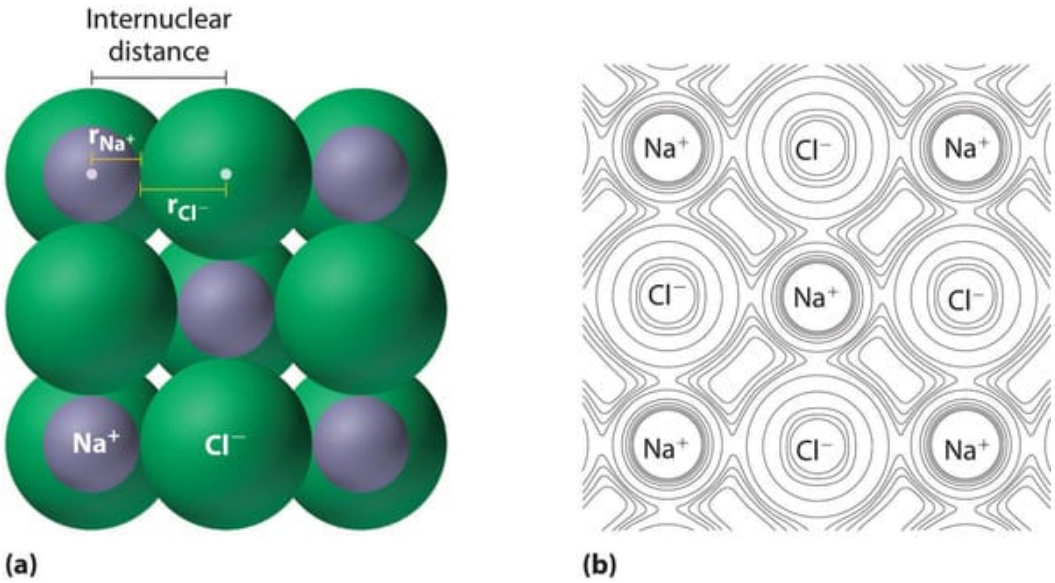


Figure 7.3.6: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl^- and Na^+.

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charges anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it *is* possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius (the radius of a cation or anion) of one or both. As illustrated in Figure 7.3.6, the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na^+ ion is essentially the same in NaCl and Na_2S, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

A comparison of ionic radii with atomic radii (Figure 7.3.7) shows that *a cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom*. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases and the ion shrinks (compare Li at 167 pm with Li^+ at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe^{2+} at 78 pm with Fe^{3+} at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases and the ion expands (compare F at 42 pm with F^- at 133 pm).

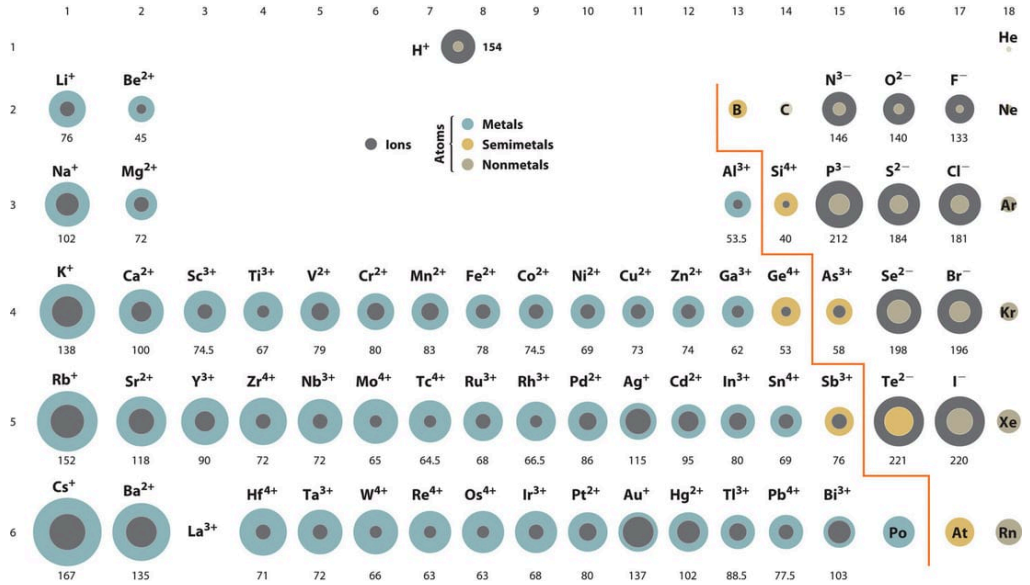


Figure 7.3.7: Ionic Radii (in Picometers) of the Most Common Ionic States of the s-, *p*-, and *d*-Block Elements.Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

Cations are **always** smaller than the neutral atom and anions are **always** larger.

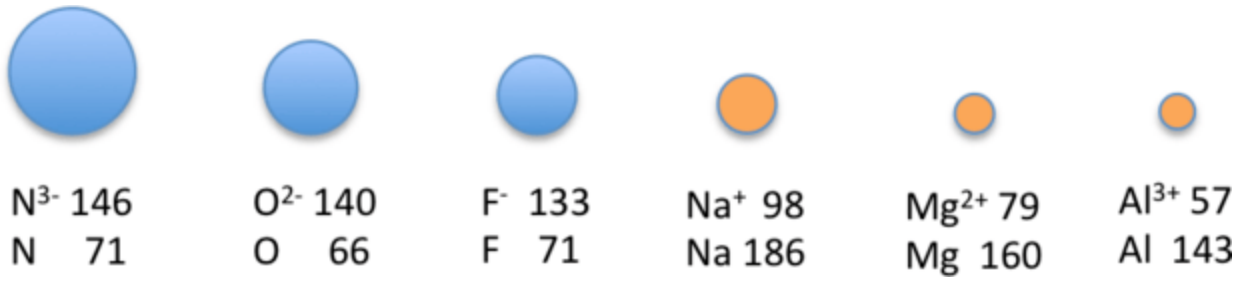
Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table 7.3.1. All three species have a nuclear charge of +11, but they contain 10 (Na^+), 11 (Na^0), and 12 (Na^-) electrons. The Na^+ ion is significantly smaller than the neutral Na atom because the $3s^1$ electron has been removed to give a closed shell with $n = 2$. The Na^- ion is larger than the parent Na atom because the additional electron produces a $3s^2$ valence electron configuration, while the nuclear charge remains the same.

Table 7.3.1: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^22s^22p^6$	$1s^22s^22p^63s^1$	$1s^22s^22p^63s^2$
Radius (pm)	102	154*	202†
***The metallic radius measured for Na(s). †Source: M. J. Wagner and J. L. Dye, "Alkalides, Electrides, and Expanded Metals," Annual Review of Materials Science 23 (1993): 225–253.**			

Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of *n* lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an **isoelectronic series**. For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^22s^22p^6$) is shown in Table 7.3.3.



The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+}. All six of the ions contain 10 electrons in the 1*s*, 2*s*, and 2*p* orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. The neon atom in this isoelectronic series is not listed in Table 7.3.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table 7.3.3: Radius of Ions with the Neon Closed-Shell Electron Configuration. Source: R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallographica 32, no. 5 (1976): 751–767.

Ion	Radius (pm)	Atomic Number
N^{3-}	146	7
O^{2-}	140	8
F^-	133	9
Na^+	98	11
Mg^{2+}	79	12
Al^{3+}	57	13

Example 7.3.2

Based on their positions in the periodic table, arrange these ions in order of increasing radius: Cl^-, K^+, S^{2-}, and Se^{2-}.

Given: four ions

Asked for: order by increasing radius

Strategy:

A. Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.
B. Determine the relative sizes of the ions based on their principal quantum numbers *n* and their locations within a row.

Solution:

A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. K^+, Cl^-, and S^{2-} form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because K^+ has the greatest nuclear charge (Z = 19), its radius is smallest, and S^{2-} with Z = 16 has the largest radius. Because selenium is directly below sulfur, we expect the Se^{2-} ion to be even larger than S^{2-}.

B The order must therefore be $K^+ < Cl^- < S^{2-} < Se^{2-}$.

Exercise 7.3.2

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br^-, Ca^{2+}, Rb^+, and Sr^{2+}.

Answer available at the end of this section.

Summary

Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges. A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius (r_{cov})** is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius (r_{met})** is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius (r_{vdW})** of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 7.3.1

$O < S < P < K$

Exercise 7.3.2

$Ca^{2+} < Sr^{2+} < Rb^+ < Br^-$

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7.4: Ionization Energy

Learning Objectives

- To correlate ionization energies with the chemistry of the elements

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. Why is this so? In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy (I) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-} \qquad \text{energy required=I} \tag{7.4.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 7.4.1 . Larger values of I mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol$$

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily. We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an nth ionization energy (I_n) according to the following reactions:

$$\mathrm{E\,(g)} \rightarrow \mathrm{E^{+}\,(g) + e^{-}} \qquad I_1 = \text{1st ionization energy} \tag{7.4.2}$$

$$\mathrm{E^{+}\,(g)} \rightarrow \mathrm{E^{2+}\,(g) + e^{-}} \qquad I_2 = \text{2nd ionization energy} \tag{7.4.3}$$

$$\mathrm{E^{2+}\,(g)} \rightarrow \mathrm{E^{3+}\,(g) + e^{-}} \qquad I_3 = \text{3rd ionization energy} \tag{7.4.4}$$

Values for the ionization energies of Li and Be listed in Table 7.4.1 show that successive ionization energies for an element increase as they go; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

Successive ionization energies for an element **increase**.

Table 7.4.1: Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Reaction	Electronic Transition	I	Reaction	Electronic Transition	I
$\mathrm{Li\ (g) \rightarrow Li^{+}\,(g) + e^{-}}$	$1s^2 2s^1 \rightarrow 1s^2$	I_1 = 520.2	$\mathrm{Be\,(g) \rightarrow Be^{+}\,(g) + e^{-}}$	$1s^2 2s^2 \rightarrow 1s^2 2s^1$	I_1 = 899.5
$\mathrm{Li^{+}\,(g) \rightarrow Li^{2+}\,(g) + e^{-}}$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$\mathrm{Be^{+}\,(g) \rightarrow Be^{2+}\,(g) + e^{-}}$	$1s^2 2s^1 \rightarrow 1s^2$	I_2 = 1757.1
$\mathrm{Li^{2+}\,(g) \rightarrow Li^{3+}\,(g) + e^{-}}$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$\mathrm{Be^{2+}\,(g) \rightarrow Be^{3+}\,(g) + e^{-}}$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$\mathrm{Be^{3+}\,(g) \rightarrow Be^{4+}\,(g) + e^{-}}$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The increase in successive ionization energies, however, is not linear, but increases drastically when removing electrons in lower n orbitals closer to the nucleus. The most important consequence of the values listed in Table 7.4.1 is that the chemistry of Li is

dominated by the Li^+ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li:

$$\mathrm{Li}^+(\mathrm{g}) \rightarrow \mathrm{Li}^{2+}(\mathrm{g}) + \mathrm{e}^- \tag{7.4.5}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be:

$$\mathrm{Be}^{2+}(\mathrm{g}) \rightarrow \mathrm{Be}^{3+}(\mathrm{g}) + \mathrm{e}^- \tag{7.4.6}$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both Li^+ and Be^{2+} have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 2s valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the 1+ ion but not the 2+ or 3+ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the 2+ ion but not the 3+ or 4+ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.

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Ionization Energy: Ionization Energy, YouTube(opens in new window) [youtu.be] (opens in new window)

Ionization Energies of *s*- and *p*-Block Elements

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of Li and Be (Table 7.4.2): successive ionization energies increase steadily as electrons are removed from the valence orbitals (3*s* or 3*p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table 7.4.2. Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from Al, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.

Table 7.4.2: Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table.Source: Data from CRC Handbook of Chemistry and Physics (2004).

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	577.4.4	1816.7	2744.8	**11,577.4.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1907.4.4	2914.1	4963.6	6274.0	**21,267.4.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,107.4.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2

***Inner-shell electron**

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3
***Inner-shell electron**							

Example 7.4.1: Highest Fourth Ionization Energy

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

a. List the electron configuration of each element.
b. Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

- B: [He]$2s^2 2p^1$
- C: [He]$2s^2 2p^2$
- N: [He]$2s^2 2p^3$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:

$$E^{3+}_{(g)} \rightarrow E^{4+}_{(g)} + e^-$$

Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

Exercise 7.4.1: Lowest Second Ionization Energy

From their locations in the periodic table, predict which of these elements has the lowest second ionization energy: Sr, Rb, or Ar.

Answer available at the end of this section.

The first column of data in Table 7.4.2 shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects represent two sides of the same coin: stronger electrostatic interactions between the electrons and the nucleus further increase the energy required to remove the electrons.

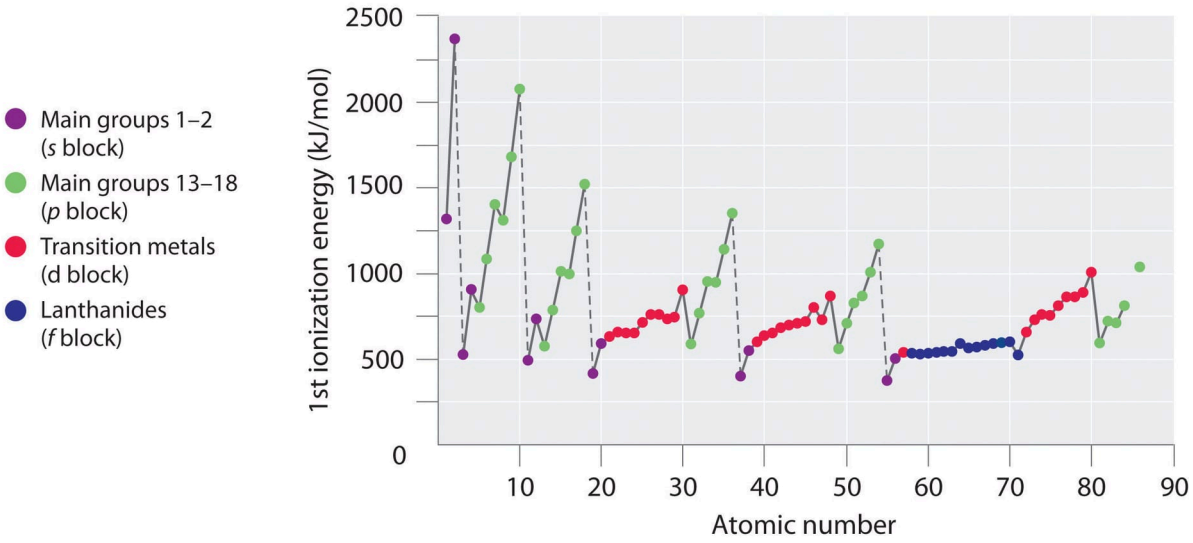


Figure 7.4.1: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

the main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electron configurations of these "exceptions" provide the answer why. The electrons in aluminum's filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the s electrons penetrate closer to the nucleus than the *p* electron does and the *p* electron is more easily removed. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

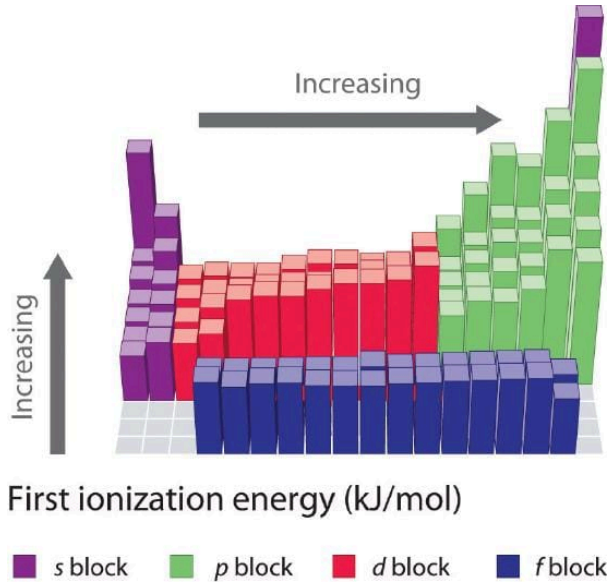


Figure 7.4.2: First Ionization Energies of the s-, *p*-, *d*-, and *f*-Block Elements

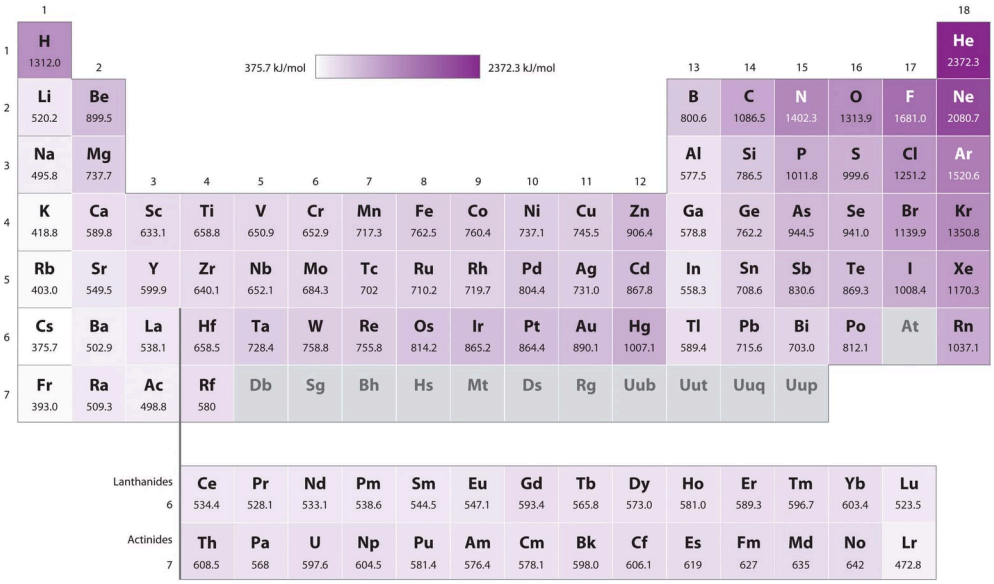
The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. First ionization energy increase from left to right and from bottom to top.

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 7.4.1 and are presented numerically and graphically in Figure 7.4.2. These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the *s* and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the

transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12).

2. First ionization energies generally decrease down a column. Although the principal quantum number n increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius typically corresponds to a lower ionization energy*.
3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).



The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.

Gallium (Ga), which is the first element following the first row of transition metals, has the following electron configuration: $[Ar]4s^23d^{10}4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the $4p$ subshell, shielding the single $4p$ electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its $[Ar]3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier p-block elements. They are sometimes referred to as *pseudo noble gas configurations*. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the $(n-1)d^{10}$ filled subshell.*

Ionization Energies of Transition Metals & Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the s- and p-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the ns electrons before the $(n-1)d$ or $(n-2)f$ electrons, respectively. This means that transition metal cations have $(n-1)d^n$ valence electron configurations, and lanthanide cations have $(n-2)f^n$ valence electron configurations. Because the $(n-1)d$ and $(n-2)f$ shells are closer to the nucleus than the ns shell, the $(n-1)d$ and $(n-2)f$ electrons screen the ns electrons quite effectively, reducing the effective nuclear charge felt by the ns electrons. As Z increases, the increasing positive charge is largely canceled by the electrons added to the $(n-1)d$ or $(n-2)f$ orbitals.

That the ns electrons are removed before the $(n-1)d$ or $(n-2)f$ electrons may surprise you because the orbitals were filled in

the reverse order. In fact, the *n*s, the (*n* – 1)*d*, and the (*n* – 2)*f* orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the *d* orbitals are filled, the effective nuclear charge causes the 3*d* orbitals to be slightly lower in energy than the 4*s* orbitals. The [Ar]$3d^2$ electron configuration of Ti^{2+} tells us that the 4*s* electrons of titanium are lost before the 3*d* electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an (*n* – 2)f^n valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

Example 7.4.2: Lowest First Ionization Energy

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

Exercise 7.4.2: Highest First Ionization Energy

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer available at the end of this section.

Summary

The tendency of an element to lose electrons is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (*I*)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting ion.

Answers

Exercise 7.4.1: Lowest Second Ionization Energy

Sr

Exercise 7.4.2: Highest First Ionization Energy

As

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7.5: Electron Affinities

Learning Objectives

- To master the concept of electron affinity as a measure of the energy required to add an electron to an atom or ion.
- To recognize the inverse relationship of ionization energies and electron affinities

The electron affinity (EA) of an element E is defined as the energy change that occurs when an electron is added to a gaseous atom or ion:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change}=EA \tag{7.5.1}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released (Figure 7.5.1).

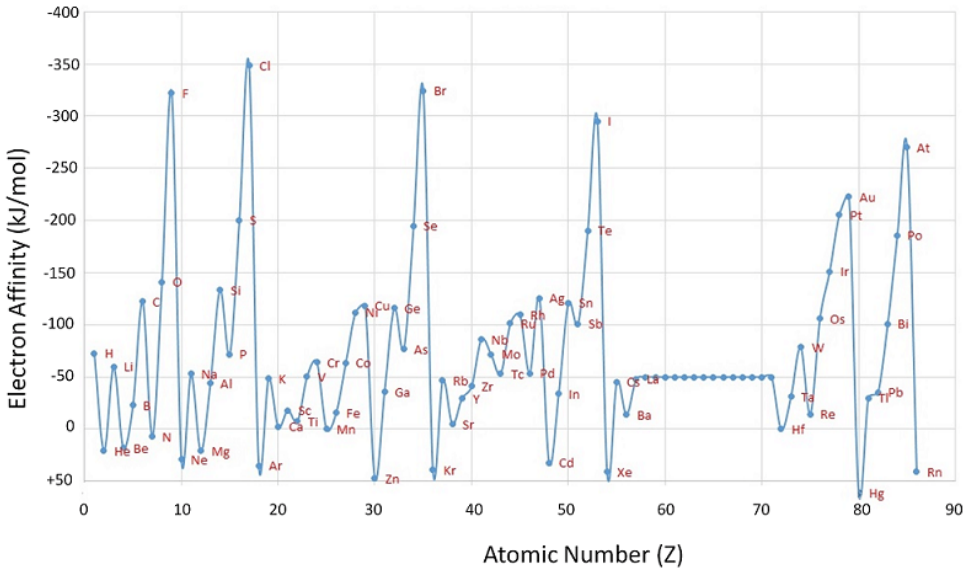


Figure 7.5.1: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies).

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

\[\ce{ Cl(g) + e^- \rightarrow Cl^- (g)} \;\;\;\; EA=-346\; kJ/mol \label{7.5.2} \]

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$\mathrm{Be\,(g) + e^-} \rightarrow \mathrm{Be^-\,(g)} \qquad EA \geq 0 \tag{7.5.2}$$

Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy:

$$\mathrm{N\,(g) + e^-} \rightarrow \mathrm{N^-\,(g)} \qquad EA \approx 0 \tag{7.5.3}$$

Generally, electron affinities become more negative across a row of the periodic table.

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because

as *n* increases, the extra electrons enter orbitals that are increasingly far from the nucleus.

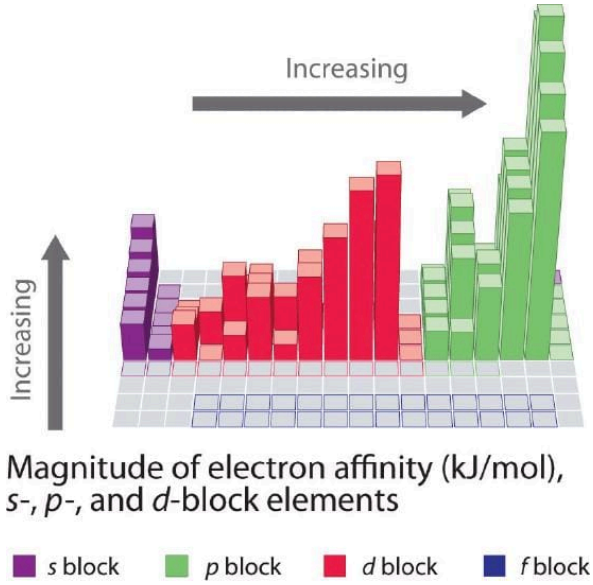


Figure 7.5.2: Electron Affinities (in kJ/mol) of the s-, *p*-, and *d*-Block Elements.

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electron affinity increases from left to right and bottom to top.

Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* negative than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small 2*p* orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row ($n = 3$) have the most negative electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.
2. The electron affinities of the alkaline earth metals become more negative from Be to Ba. The energy separation between the filled ns^2 and the empty *np* subshells decreases with increasing *n*, so that formation of an anion from the heavier elements becomes energetically more favorable.

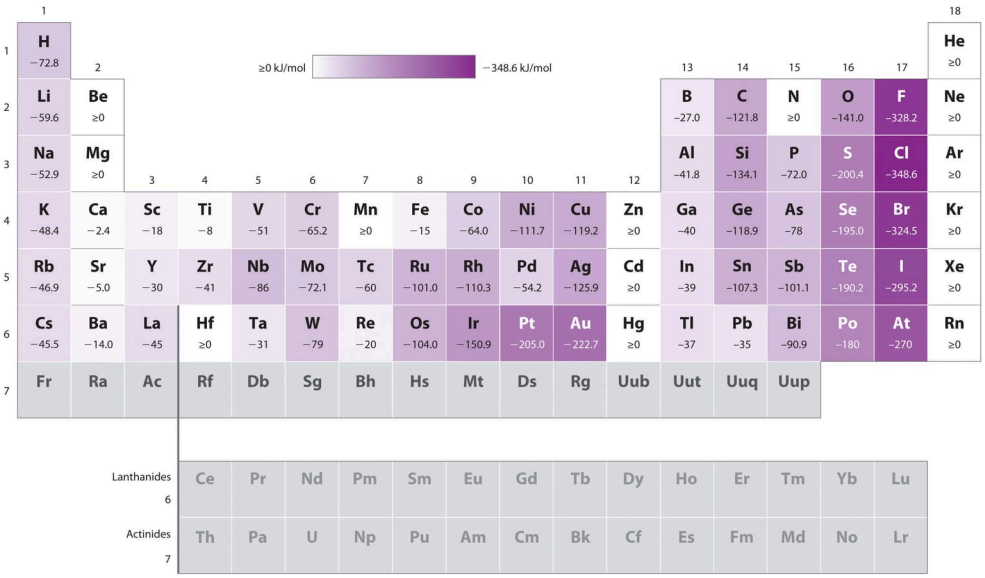


Figure 7.5.3: There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from *Journal of Physical and Chemical Reference Data* 28, no. 6 (1999).

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA_1 \tag{7.5.4}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change} = EA_2 \tag{7.5.5}$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is –141 kJ/mol, but the second electron affinity is +744 kJ/mol:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{7.5.6}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{7.5.7}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{7.5.8}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.

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Electron Affinity: Electron Affinity, YouTube(opens in new window) [youtu.be] (opens in new window)

If energy is required to form both positively charged cations and monatomic polyanions, why do ionic compounds such as MgO, Na_2S, and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt*.

Example 7.5.1: Contrasting Electron Affinities of Sb, Se, and Te

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.
B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

A We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

Exercise 7.5.1: Contrasting Electron Affinities of Rb, Sr, and Xe

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer available at the end of this section.

Summary

The **electron affinity** (*EA*) of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table.

Answers

Exercise 7.5.1: Contrasting Electron Affinities of Rb, Sr, and Xe

Rb

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7.6: Metals, Nonmetals, and Metalloids

Learning Objectives

- To understand the basic properties separating Metals from Nonmetals and Metalloids

An element is the simplest form of matter that cannot be split into simpler substances or built from simpler substances by any ordinary chemical or physical method. There are 118 elements known to us, out of which 92 are naturally occurring, while the rest have been prepared artificially. Elements are further classified into metals, non-metals, and metalloids based on their properties, which are correlated with their placement in the periodic table.

Table 7.6.1: Characteristic properties of metallic and non-metallic elements:

Metallic Elements	Nonmetallic elements
Distinguishing luster (shine)	Non-lustrous, various colors
Malleable and ductile (flexible) as solids	Brittle, hard or soft
Conduct heat and electricity	Poor conductors
Metallic oxides are basic, ionic	Nonmetallic oxides are acidic, covalent
Form cations in aqueous solution	Form anions, oxyanions in aqueous solution

Metals

With the exception of hydrogen, all elements that form positive ions by losing electrons during chemical reactions are called metals. Thus metals are electropositive elements with relatively low ionization energies. They are characterized by bright luster, hardness, ability to resonate sound and are excellent conductors of heat and electricity. Metals are solids under normal conditions except for Mercury.

Physical Properties of Metals

Metals are lustrous, malleable, ductile, good conductors of heat and electricity. Other properties include:

- **State**: Metals are solids at room temperature with the exception of mercury, which is liquid at room temperature (Gallium is liquid on hot days).
- **Luster**: Metals have the quality of reflecting light from their surface and can be polished e.g., gold, silver and copper.
- **Malleability:** Metals have the ability to withstand hammering and can be made into thin sheets known as foils. For example, a sugar cube sized chunk of gold can be pounded into a thin sheet that will cover a football field.
- **Ductility:** Metals can be drawn into wires. For example, 100 g of silver can be drawn into a thin wire about 200 meters long.
- **Hardness:** All metals are hard except sodium and potassium, which are soft and can be cut with a knife.
- **Valency:** Metals typically have 1 to 3 electrons in the outermost shell of their atoms.
- **Conduction**: Metals are good conductors because they have free electrons. Silver and copper are the two best conductors of heat and electricity. Lead is the poorest conductor of heat. Bismuth, mercury and iron are also poor conductors
- **Density**: Metals have high density and are very heavy. Iridium and osmium have the highest densities whereas lithium has the lowest density.
- **Melting and Boiling Points**: Metals have high melting and boiling points. Tungsten has the highest melting and boiling points whereas mercury has the lowest. Sodium and potassium also have low melting points.

Chemical Properties of Metals

Metals are electropositive elements that generally form *basic* or *amphoteric* oxides with oxygen. Other chemical properties include:

- **Electropositive Character**: Metals tend to have low ionization energies, and *typically lose electrons (i.e. are **oxidized**) when they undergo chemical reactions* They normally do not accept electrons. For example:
  - Alkali metals are always 1^+ (lose the electron in s subshell)
  - Alkaline earth metals are always 2^+ (lose both electrons in s subshell)
  - Transition metal ions do not follow an obvious pattern, 2^+ is common (lose both electrons in s subshell), and 1^+ and 3^+ are also observed

$$\mathrm{Na^0} \rightarrow \mathrm{Na^+ + e^-} \tag{7.6.1}$$

$$\mathrm{Mg^0} \rightarrow \mathrm{Mg^{2+} + 2\,e^-} \tag{7.6.2}$$

$$\mathrm{Al^0} \rightarrow \mathrm{Al^{3+} + 3\,e^-} \tag{7.6.3}$$

Compounds of metals with non-metals tend to be ***ionic*** in nature. Most metal oxides are basic oxides and dissolve in water to form ***metal hydroxides***:

$$\mathrm{Na_2O\,(s) + H_2O\,(l)} \rightarrow \mathrm{2\,NaOH\,(aq)} \tag{7.6.4}$$

$$\mathrm{CaO\,(s) + H_2O\,(l)} \rightarrow \mathrm{Ca(OH)_2\,(aq)} \tag{7.6.5}$$

Metal oxides exhibit their ***basic*** chemical nature by reacting with ***acids*** to form metal ***salts*** and water:

$$\mathrm{MgO\,(s) + HCl\,(aq)} \rightarrow \mathrm{MgCl_2\,(aq) + H_2O\,(l)} \tag{7.6.6}$$

$$\mathrm{NiO\,(s) + H_2SO_4\,(aq)} \rightarrow \mathrm{NiSO_4\,(aq) + H_2O\,(l)} \tag{7.6.7}$$

Example 7.6.1

What is the chemical formula for aluminum oxide?

Solution

Al has a 3+ charge, the oxide ion is O^{2-}, thus Al_2O_3.

Example 7.6.2

Would you expect it to be solid, liquid or gas at room temperature?

Solutions

Oxides of metals are characteristically solid at room temperature

Example 7.6.3

Write the balanced chemical equation for the reaction of aluminum oxide with nitric acid:

Solution

Metal oxide + acid -> salt + water

$$\mathrm{Al_2O_3\,(s) + 6\,HNO_3\,(aq)} \rightarrow \mathrm{2\,Al(NO_3)_3\,(aq) + 3\,H_2O\,(l)}$$

Nonmetals

Elements that tend to gain electrons to form anions during chemical reactions are called non-metals. These are electronegative elements with high ionization energies. They are non-lustrous, brittle and poor conductors of heat and electricity (except graphite).

Non-metals can be gases, liquids or solids.

Physical Properties of Nonmetals

- **Physical State**: Most of the non-metals exist in two of the three states of matter at room temperature: gases (oxygen) and solids (carbon). Only bromine exists as a liquid at room temperature.
- **Non-Malleable and Ductile**: Non-metals are very brittle, and cannot be rolled into wires or pounded into sheets.
- **Conduction**: They are poor conductors of heat and electricity.
- **Luster:** These have no metallic luster and do not reflect light.
- **Melting and Boiling Points**: The melting points of non-metals are *generally* lower than metals, but are highly variable.
- Seven non-metals exist under standard conditions as *diatomic molecules*: $\mathrm{H_2\,(g)}$, $\mathrm{N_2\,(g)}$, $\mathrm{O_2\,(g)}$, $\mathrm{F_2\,(g)}$, $\mathrm{Cl_2\,(g)}$, $\mathrm{Br_2\,(l)}$, $\mathrm{I_2\,(s)}$.

Chemical Properties of Nonmetals

Non-metals have a tendency to gain or share electrons with other atoms. They are electronegative in character. Nonmetals, when reacting with metals, tend to gain electrons (typically *attaining noble gas electron configuration)* and become ***anions:***

$$\mathrm{3\,Br_2\,(l) + 2\,Al\,(s)\ \rightarrow 2\,AlBr_3\,(s)}$$

Compounds composed entirely of nonmetals are covalent substances. They generally form acidic or neutral oxides with oxygen that that dissolve in water to form acids:

$$\mathrm{CO_2\,(g) + H_2O\,(l) \rightarrow \underset{\text{carbonic acid}}{H_2CO_3\,(aq)}}$$

As you may know, carbonated water is slightly acidic (carbonic acid).

Nonmetal oxides can combine with bases to form salts.

$$\mathrm{CO_2\,(g) + 2\,NaOH\,(aq)\ \rightarrow Na_2CO_3\,(aq) + H_2O\,(l)}$$

Metalloids

Metalloids have properties intermediate between the metals and nonmetals. Metalloids are useful in the semiconductor industry. Metalloids are all solid at room temperature. They can form alloys with other metals. Some metalloids, such as silicon and germanium, can act as electrical conductors under the right conditions, thus they are called semiconductors. Silicon for example appears lustrous, but is *not* malleable nor ductile (it is *brittle* - a characteristic of some nonmetals). It is a much poorer conductor of heat and electricity than the metals. The physical properties of metalloids tend to be metallic, but their chemical properties tend to be non-metallic. The oxidation number of an element in this group can range from +5 to -2, depending on the group in which it is located.

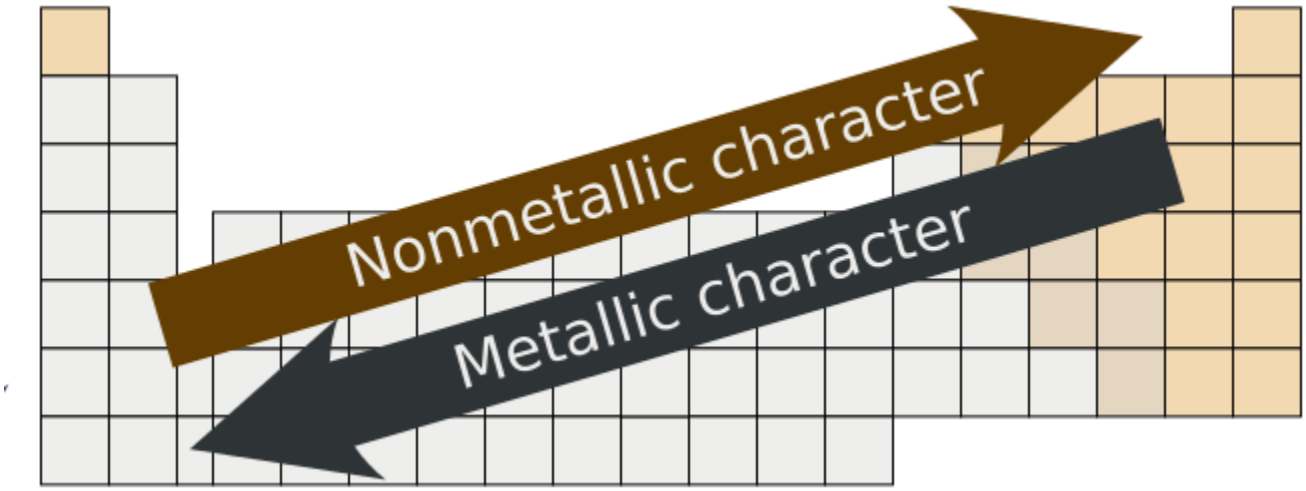
Table 7.6.2: Elements categorized into metals, non-metals and metalloids.

Metals	Non-metals	Metalloids
Gold	Oxygen	Silicon
Silver	Carbon	Boron
Copper	Hydrogen	Arsenic
Iron	Nitrogen	Antimony
Mercury	Sulfur	Germanium
Zinc	Phosphorus	

Trends in Metallic and Nonmetallic Character

Metallic character is strongest for the elements in the leftmost part of the periodic table, and tends to decrease as we move to

the right in any period (nonmetallic character increases with increasing electronegativity and ionization energy values). Within any group of elements (columns), the metallic character increases from top to bottom (the electronegativity and ionization energy values generally decrease as we move down a group). This general trend is not necessarily observed with the transition metals.



Non metallic character increases bottom to top and left to right with the most nonmetal element in the top right corner. metallic character shows the opposite trend with the most metallic element being in the bottom left.

Contributors and Attributions

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7.7: Group Trends for the Active Metals

The elements within the same group of the periodic table tend to exhibit similar physical and chemical properties. Four major factors affect reactivity of metals: nuclear charge, atomic radius, shielding effect and sublevel arrangement (of electrons). Metal reactivity relates to ability to lose electrons (oxidize), form basic hydroxides, form ionic compounds with non-metals. In general, the bigger the atom, the greater the ability to lose electrons. The greater the shielding, the greater the ability to lose electrons. Therefore, metallic character increases going down the table, and decreases going across -- so the most active metal is towards the left and down.

Group 1: The Alkali Metals

The word "alkali" is derived from an Arabic word meaning "ashes". Many sodium and potassium compounds were isolated from wood ashes ($\mathrm{Na_2CO_3}$ and $\mathrm{K_2CO_3}$ are still occasionally referred to as "soda ash" and "potash"). In the alkali group, as we go down the group we have elements Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs) and Francium (Fr). Several physical properties of these elements are compared in Table 7.7.1. These elements have all only one electron in their outermost shells. All the elements show metallic properties and have valence +1, hence they give up electron easily.

Table 7.7.1: General Properties of Group I Metals

Element	Electronic Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius	Ionization Energy (kJ/mol)
Lithium	$[He]2s^1$	181	0.53	1.52	520
Sodium	$[Ne]3s^1$	98	0.97	1.86	496
Potassium	$[Ar]4s^1$	63	0.86	2.27	419
Rubidium	$[Kr]5s^1$	39	1.53	2.47	403
Cesium	$[Xe]6s^1$	28	1.88	2.65	376

As we move down the group (from Li to Fr), the following trends are observed (Table 7.7.1):

- All have a single electron in an 's' valence orbital
- The melting point decreases
- The density increases
- The atomic radius increases
- The ionization energy decreases (first ionization energy)

    The alkali metals have the lowest I_1 values of the elements

This represents the relative ease with which the lone electron in the outer 's' orbital can be removed.

The alkali metals are very reactive, readily losing 1 electron to form an ion with a 1+ charge:

$$M \rightarrow M^+ + e-$$

Due to this reactivity, the alkali metals are found in nature only as compounds. The alkali metals combine directly with most nonmetals:

- React with hydrogen to form solid *hydrides*

$$2M_{(s)} + H_{2(g)} \rightarrow 2MH(s)$$

(Note: hydrogen is present in the metal hydride as the ***hydride*** H^- ion)

- React with sulfur to form solid *sulfides*

$$2M_{(s)} + S_{(s)} \rightarrow M_2S_{(s)}$$

React with chlorine to form solid *chlorides*

$$2M_{(s)} + Cl_{2(g)} \rightarrow 2MCl_{(s)}$$

Alkali metals react with water to produce hydrogen gas and alkali metal hydroxides; this is a very exothermic reaction (Figure 7.7.1).

$$2M_{(s)} + 2H_2O_{(l)} \rightarrow 2MOH_{(aq)} + H_{2(g)}$$

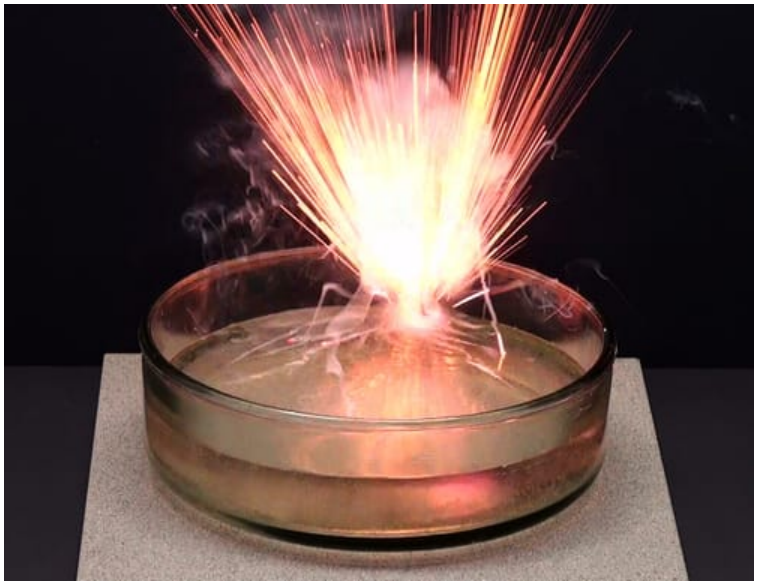


Figure 7.7.1: A small piece of potassium metal explodes as it reacts with water. (CC SA-BY 3.0; Tavoromann)

The reaction between alkali metals and oxygen is more complex:

- A common reaction is to form metal oxides which contain the ***O^{2-} ion***

$$4Li_{(s)} + O_{2(g)} \rightarrow \underbrace{2Li_2O_{(s)}}_{\text{lithium oxide}}$$

Other alkali metals ***can*** form metal peroxides (contains O_2^{2-} ion)

$$2Na(s) + O_{2(g)} \rightarrow \underbrace{Na_2O_{2(s)}}_{\text{sodium peroxide}}$$

K, Rb and Cs ***can*** also form superoxides (O_2^- ion)

$$K(s) + O_{2(g)} \rightarrow \underbrace{KO_{2(s)}}_{\text{potassium superoxide}}$$

Colors via Absorption

The color of a chemical is produced when a valence electron in an atom is excited from one energy level to another by visible radiation. In this case, the particular frequency of light that excites the electron is ***absorbed***. Thus, the remaining light that you see is white light devoid of one or more wavelengths (thus appearing colored). Alkali metals, having lost their outermost electrons, have no electrons that can be excited by visible radiation. Alkali metal salts and their aqueous solution are colorless unless they contain a colored anion.

Colors via Emission

When alkali metals are placed in a flame the ions are reduced (gain an electron) in the lower part of the flame. The electron is excited (jumps to a higher orbital) by the high temperature of the flame. When the excited electron falls back down to a lower orbital a photon is released. The transition of the valence electron of sodium from the 3p down to the 3s subshell results in release of a photon with a wavelength of 589 nm (yellow)

Flame colors:

- Lithium: crimson red
- Sodium: yellow
- Potassium: lilac

Group 2: The Alkaline Earth Metals

Compared with the alkali metals, the alkaline earth metals are typically harder, more dense, melt at a higher temperature. The first ionization energies (I_1) of the alkaline earth metals are not as low as the alkali metals. The alkaline earth metals are therefore less reactive than the alkali metals (Be and Mg are the least reactive of the alkaline earth metals). Several physical properties of these elements are compared in Table 7.7.2.

Table 7.7.2: General Properties of Group 2 Metals

Element	Electronic Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius	Ionization Energy (kJ/mol)
Beryllium	$[He]2s^2$	1278	1.85	1.52	899
Magnesium	$[Ne]3s^2$	649	1.74	1.60	738
Calcium	$[Ar]4s^2$	839	1.54	1.97	590
Strontium	$[Kr]5s^2$	769	2.54	2.15	549
Barium	$[Xe]6s^2$	725	3.51	2.17	503

Calcium, and elements below it, react readily with water at room temperature:

$$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$

The tendency of the alkaline earths to lose their two valence electrons is demonstrated in the reactivity of Mg towards chlorine gas and oxygen:

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$

$$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$

The 2+ ions of the alkaline earth metals have a noble gas like electron configuration and are thus form colorless or white compounds (unless the anion is itself colored). Flame colors:

- Calcium: brick red
- Strontium: crimson red
- Barium: green

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7.8: Group Trends for Selected Nonmetals

Learning Objectives

- To gain a descriptive understanding of the chemical properties of Hydrogen, the group 16, 17 and 18 elements.

Non-metallic character is the ability to be reduced (be an oxidizing agent), form acidic hydroxides, form covalent compounds with non-metals. These characteristics increase with a larger nuclear charge and smaller radius, with no increase in shielding. The most active non-metal would be the one farthest up and to the right -- not including the noble gases (non-reactive.)

Hydrogen

Hydrogen has a $1s^1$ electron configuration and is placed above the alkali metal group. Hydrogen is a ***non-metal***, which occurs as a ***gas*** (H_2) under normal conditions.

- Its ionization energy is considerably higher (due to lack of shielding, and thus higher Z_{eff}) than the rest of the Group 1 metals and is more like the ***nonmetals***
- Hydrogen generally reacts with other nonmetals to form molecular compounds (typically highly exothermic)
- Hydrogen reacts with active metals to form metal hydrides which contain the ***H^- hydride ion***:

$$2Na_{(s)} + H_{2(g)} \rightarrow 2NaH_{(s)} \tag{7.8.1}$$

- Hydrogen can also lose an electron to yield the aqueous $H^+_{(aq)}$ hydronium ion.

Group 16: The Oxygen Family

As we proceed down group 16 the elements become more metallic in nature:

- Oxygen is a gas, the rest are solids
- Oxygen, sulfur and selenium are nonmetals
- Tellurium is a metalloid with some metal properties
- Polonium is a metal

Oxygen can be found in two molecular forms, O_2 and O_3 (ozone). These two forms of oxygen are called ***allotropes*** (*different forms of the same element in the same state*)

$$3O_{2(g)} \rightarrow 2O_{3(g)} \quad \Delta H = 284.6\ kJ/mol \tag{7.8.2}$$

the reaction is endothermic, thus ozone is less stable that O_2

> Oxygen has a great tendency to attract electrons from other elements (i.e. to "oxidize" them)

- Oxygen in combination with metals is almost always present as the O^{2-} ion (which has noble gas electronic configuration and is particularly stable)
- Two other oxygen anions are observed: ***peroxide (O_2^{2-}) and superoxide (O_2^-)***

Sulfur

Sulfur also exists in several allotropic forms, the most common stable allotrope is the yellow solid S_8 (an 8 member ring of sulfur atoms). Like oxygen, ***sulfur has a tendency to gain electrons*** from other elements, and to form ***sulfides*** (which contain the S^{2-} ion). This is particular true for the active metals:

$$16Na_{(s)} + S_{8(s)} \rightarrow 8Na_2S_{(s)} \tag{7.8.3}$$

Note: most sulfur in nature is present as a metal-sulfur compound. Sulfur chemistry is more complex than that of oxygen.

Group 17: The Halogens

"Halogen" is derived from the Greek meaning "salt formers"

- Astatine is radioactive and rare, and some of its properties are unknown
- All the halogens are ***nonmetals***
- Each element consists of diatomic molecules under standard conditions

Colors of diatomic halogens: (*not* flame colors)

- Fluorine: pale yellow
- Chlorine: yellow green
- Bromine: reddish brown
- Iodine: violet vapor

The halogens have some of the most negative electron affinities (i.e. large exothermic process in gaining an electron from another element)

$$X_2 + 2e^- \rightarrow 2X^- \tag{7.8.4}$$

- Fluorine and chlorine are the most reactive halogens (highest electron affinities). Fluorine will remove electrons from almost any substance (including several of the noble gases from Group 18).

> **Note**
>
> The chemistry of the halogens is dominated by their tendency to gain electrons from other elements (forming a halide ion)

In 1992, **22.3 billion pounds** of chlorine was produced. Both chlorine and sodium can be produced by electrolysis of molten sodium chloride (table salt). The electricity is used to strip electrons from chloride ions and transfer them to sodium ions to produce chlorine gas and solid sodium metal

Chlorine reacts slowly with water to produce hydrochloric acid and hypochlorous acid:

$$Cl_{2(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)} + HOCl_{(aq)}.5 \tag{7.8.5}$$

Hypochlorous acid is a disinfectant, thus chlorine is a useful addition to swimming pool water

The halogens react with most metals to form ionic halides:

$$Cl_{2(g)} + 2Na_{(s)} \rightarrow 2NaCl_{(s)} \tag{7.8.6}$$

Group 18: The Noble Gases

- Nonmetals
- Gases at room temperature
- monoatomic
- completely filled 's' and 'p' subshells
- large first ionization energy, ***but this decreases somewhat as we move down the group***

Rn is highly radioactive and some of its properties are unknown

They are exceptionally unreactive. It was reasoned that if any of these were reactive, they would most likely be Rn, Xe or Kr where the first ionization energies were lower.

Note

In order to react, they would have to be combined with an element which had a high tendency to remove electrons from other atoms. Such as fluorine.

Compounds of noble gases to date:

$$XeF_2\ XeF_4\ XeF_6$$

only one compound with Kr has been made

$$KrF_2$$

No compounds observed with He, Ne, or Ar; they are truly inert gases.

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7.E: Periodic Properties of the Elements (Exercises)

7.1: Development of the Periodic Table

Conceptual Problems

1. Johannes Dobereiner is credited with developing the concept of chemical triads. Which of the group 15 elements would you expect to compose a triad? Would you expect B, Al, and Ga to act as a triad? Justify your answers.
2. Despite the fact that Dobereiner, Newlands, Meyer, and Mendeleev all contributed to the development of the modern periodic table, Mendeleev is credited with its origin. Why was Mendeleev's periodic table accepted so rapidly?
3. How did Moseley's contribution to the development of the periodic table explain the location of the noble gases?
4. The *eka*- naming scheme devised by Mendeleev was used to describe undiscovered elements.
    1. Use this naming method to predict the atomic number of *eka*-mercury, *eka*-astatine, *eka*-thallium, and *eka*-hafnium.
    2. Using the *eka*-prefix, identify the elements with these atomic numbers: 79, 40, 51, 117, and 121.

Numerical Problem

1. Based on the data given, complete the table.

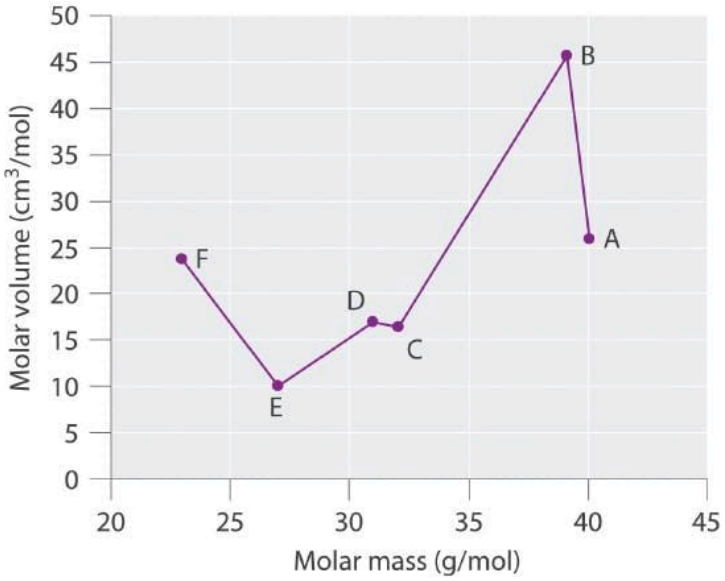
Species	Molar Mass (g/mol)	Density (g/cm3)	Molar Volume (cm3/mol)
A	40.078		25.85
B	39.09	0.856	
C	32.065		16.35
D		1.823	16.98
E	26.98		9.992
F	22.98	0.968	

Plot molar volume versus molar mass for these substances. According to Meyer, which would be considered metals and which would be considered nonmetals?

Numerical Answer

1.

Species	Molar Mass (g/mol)	Density (g/cm^3)	Molar Volume (cm^3/mol)
A	**40.078**	1.550	**25.85**
B	**39.09**	**0.856**	45.67
C	**32.065**	1.961	**16.35**
D	30.95	**1.823**	**16.98**
E	**26.98**	2.700	**9.992**
F	**22.98**	**0.968**	23.7



2. Meyer found that the alkali metals had the highest molar volumes, and that molar volumes decreased steadily with increasing atomic mass, then leveled off, and finally rose again. The elements located on the rising portion of a plot of molar volume versus molar mass were typically nonmetals. If we look at the plot of the data in the table, we can immediately identify those elements with the largest molar volumes (A, B, F) as metals located on the left side of the periodic table. The element with the smallest molar volume (E) is aluminum. The plot shows that the subsequent elements (C, D) have molar volumes that are larger than that of E, but smaller than those of A and B. Thus, C and D are most likely to be nonmetals (which is the case: C = sulfur, D = phosphorus).

7.2: Effective Nuclear Charge

Conceptual Problems

1. What happens to the energy of a given orbital as the nuclear charge Z of a species increases? In a multielectron atom and for a given nuclear charge, the Z_{eff} experienced by an electron depends on its value of l. Why?

2. The electron density of a particular atom is divided into two general regions. Name these two regions and describe what each represents.

3. As the principal quantum number increases, the energy difference between successive energy levels decreases. Why? What would happen to the electron configurations of the transition metals if this decrease did not occur?

4. Describe the relationship between electron shielding and Z_{eff} on the outermost electrons of an atom. Predict how chemical reactivity is affected by a decreased effective nuclear charge.

5. If a given atom or ion has a single electron in each of the following subshells, which electron is easier to remove?

    - 2*s*, 3s
    - 3*p*, 4*d*
    - 2*p*, 1s
    - 3*d*, 4s

7.3: Sizes of Atoms and Ions

Conceptual Problems

1. The electrons of the 1s shell have a stronger electrostatic attraction to the nucleus than electrons in the 2s shell. Give two

reasons for this.

2. Predict whether Na or Cl has the more stable $1s^2$ shell and explain your rationale.
3. Arrange K, F, Ba, Pb, B, and I in order of decreasing atomic radius.
4. Arrange Ag, Pt, Mg, C, Cu, and Si in order of increasing atomic radius.
5. Using the periodic table, arrange Li, Ga, Ba, Cl, and Ni in order of increasing atomic radius.
6. Element M is a metal that forms compounds of the type MX_2, MX_3, and MX_4, where X is a halogen. What is the expected trend in the ionic radius of M in these compounds? Arrange these compounds in order of decreasing ionic radius of M.
7. The atomic radii of Na and Cl are 190 and 79 pm, respectively, but the distance between sodium and chlorine in NaCl is 282 pm. Explain this discrepancy.
8. Are shielding effects on the atomic radius more pronounced across a row or down a group? Why?
9. What two factors influence the size of an ion relative to the size of its parent atom? Would you expect the ionic radius of S^{2-} to be the same in both MgS and Na_2S? Why or why not?
10. Arrange Br^-, Al^{3+}, Sr^{2+}, F^-, O^{2-}, and I^- in order of increasing ionic radius.
11. Arrange P^{3-}, N^{3-}, Cl^-, In^{3+}, and S^{2-} in order of decreasing ionic radius.
12. How is an isoelectronic series different from a series of ions with the same charge? Do the cations in magnesium, strontium, and potassium sulfate form an isoelectronic series? Why or why not?
13. What isoelectronic series arises from fluorine, nitrogen, magnesium, and carbon? Arrange the ions in this series by
    1. increasing nuclear charge.
    2. increasing size.
14. What would be the charge and electron configuration of an ion formed from calcium that is isoelectronic with
    1. a chloride ion?
    2. Ar^+?

Conceptual Answers

1. The 1s shell is closer to the nucleus and therefore experiences a greater electrostatic attraction. In addition, the electrons in the 2s subshell are shielded by the filled $1s^2$ shell, which further decreases the electrostatic attraction to the nucleus.
2.
3. Ba > K > Pb > I > B > F
4.
5.
6.
7. The sum of the calculated atomic radii of sodium and chlorine *atoms* is 253 pm. The sodium cation is significantly smaller than a neutral sodium atom (102 versus 154 pm), due to the loss of the single electron in the 3s orbital. Conversely, the chloride ion is much larger than a neutral chlorine atom (181 versus 99 pm), because the added electron results in greatly increased electron–electron repulsions within the filled $n = 3$ principal shell. Thus, transferring an electron from sodium to chlorine decreases the radius of sodium by about 50%, but causes the radius of chlorine to almost double. The net effect is that the distance between a sodium ion and a chloride ion in NaCl is *greater* than the sum of the atomic radii of the neutral atoms.

Numerical Problems

1. Plot the ionic charge versus ionic radius using the following data for Mo: Mo^{3+}, 69 pm; Mo^{4+}, 65 pm; and Mo^{5+}, 61 pm. Then use this plot to predict the ionic radius of Mo^{6+}. Is the observed trend consistent with the general trends discussed in the chapter? Why or why not?

2. Internuclear distances for selected ionic compounds are given in the following table.

    1. If the ionic radius of Li^+ is 76 pm, what is the ionic radius of each of the anions?

	LiF	LiCl	LiBr	LiI
Distance (pm)	209	257	272	296

- What is the ionic radius of Na^+?

	NaF	NaCl	NaBr	NaI
Distance (pm)	235	282	298	322

- Arrange the gaseous species Mg^{2+}, P^{3-}, Br^-, S^{2-}, F^-, and N^{3-} in order of increasing radius and justify your decisions.

7.4: Ionization Energy

Conceptual Problems

1. Identify each statement as either true or false and explain your reasoning.

    a. Ionization energies increase with atomic radius.
    b. Ionization energies decrease down a group.
    c. Ionization energies increase with an increase in the magnitude of the electron affinity.
    d. Ionization energies decrease diagonally across the periodic table from He to Cs.
    e. Ionization energies depend on electron configuration.
    f. Ionization energies decrease across a row.

2. Based on electronic configurations, explain why the first ionization energies of the group 16 elements are lower than those of the group 15 elements, which is contrary to the general trend.

3. The first through third ionization energies do not vary greatly across the lanthanides. Why? How does the effective nuclear charge experienced by the ns electron change when going from left to right (with increasing atomic number) in this series?

4. Most of the first row transition metals can form at least two stable cations, for example iron(II) and iron(III). In contrast, scandium and zinc each form only a single cation, the Sc^{3+} and Zn^{2+} ions, respectively. Use the electron configuration of these elements to provide an explanation.

5. Of the elements Nd, Al, and Ar, which will readily form(s) +3 ions? Why?

6. Orbital energies can reverse when an element is ionized. Of the ions B^{3+}, Ga^{3+}, Pr^{3+}, Cr^{3+}, and As^{3+}, in which would you expect this reversal to occur? Explain your reasoning.

7. The periodic trends in electron affinities are not as regular as periodic trends in ionization energies, even though the processes are essentially the converse of one another. Why are there so many more exceptions to the trends in electron affinities compared to ionization energies?

8. Elements lying on a lower right to upper left diagonal line cannot be arranged in order of increasing electronegativity according to where they occur in the periodic table. Why?

9. Why do ionic compounds form, if energy is required to form gaseous cations?
10. Why is Pauling's definition of electronegativity considered to be somewhat limited?
11. Based on their positions in the periodic table, arrange Sb, O, P, Mo, K, and H in order of increasing electronegativity.
12. Based on their positions in the periodic table, arrange V, F, B, In, Na, and S in order of decreasing electronegativity.

Conceptual Answers

5. Both Al and Nd will form a cation with a +3 charge. Aluminum is in Group 13, and loss of all three valence electrons will produce the Al^{3+} ion with a noble gas configuration. Neodymium is a lanthanide, and all of the lanthanides tend to form +3 ions because the ionization potentials do not vary greatly across the row, and a +3 charge can be achieved with many oxidants.

11. K < Mo ≈ Sb < P ≈ H < O

Numerical Problems

1. The following table gives values of the first and third ionization energies for selected elements:

Number of Electrons	Element	I_1 ($E \rightarrow E^+ + e^-$, kJ/mol)	Element	I_3 ($E^{2+} \rightarrow E^{3+} + e^-$, kJ/mol)
11	Na	495.9	Al	2744.8
12	Mg	737.8	Si	3231.6
13	Al	577.6	P	2914.1
14	Si	786.6	S	3357
15	P	1011.9	Cl	3822
16	S	999.6	Ar	3931
17	Cl	1251.2	K	4419.6
18	Ar	1520.6	Ca	4912.4

   Plot the ionization energies versus the number of electrons. Explain why the slopes of the I_1 and I_3 plots are different, even though the species in each row of the table have the same electron configurations.

2. Would you expect the third ionization energy of iron, corresponding to the removal of an electron from a gaseous Fe^{2+} ion, to be larger or smaller than the fourth ionization energy, corresponding to the removal of an electron from a gaseous Fe^{3+} ion? Why? How would these ionization energies compare to the first ionization energy of Ca?
3. Which would you expect to have the highest first ionization energy: Mg, Al, or Si? Which would you expect to have the highest third ionization energy. Why?
4. Use the values of the first ionization energies given in Figure 7.11 to construct plots of first ionization energy versus atomic number for (a) boron through oxygen in the second period; and (b) oxygen through tellurium in group 16. Which plot shows more variation? Explain the reason for the variation in first ionization energies for this group of elements.
5. Arrange Ga, In, and Zn in order of increasing first ionization energies. Would the order be the same for second and third ionization energies? Explain your reasoning.
6. Arrange each set of elements in order of increasing magnitude of electron affinity.
   1. Pb, Bi, and Te
   2. Na, K, and Rb

3. P, C, and Ge

7. Arrange each set of elements in order of decreasing magnitude of electron affinity.

    1. As, Bi, and N
    2. O, F, and Ar
    3. Cs, Ba, and Rb

8. Of the species F, O^-, Al^{3+}, and Li^+, which has the highest electron affinity? Explain your reasoning.

9. Of the species O^-, N^{2-}, Hg^{2+}, and H^+, which has the highest electron affinity? Which has the lowest electron affinity? Justify your answers.

10. The Mulliken electronegativity of element A is 542 kJ/mol. If the electron affinity of A is –72 kJ/mol, what is the first ionization energy of element A? Use the data in the following table as a guideline to decide if A is a metal, a nonmetal, or a semimetal. If 1 g of A contains 4.85×10^{21} molecules, what is the identity of element A?

	Na	Al	Si	S	Cl
EA (kJ/mol)	–59.6	–41.8	–134.1	–200.4	–348.6
I (kJ/mol)	495.8	577.5	786.5	999.6	1251.2

11. Based on their valence electron configurations, classify the following elements as either electrical insulators, electrical conductors, or substances with intermediate conductivity: S, Ba, Fe, Al, Te, Be, O, C, P, Sc, W, Na, B, and Rb.

12. Using the data in Problem 10, what conclusions can you draw with regard to the relationship between electronegativity and electrical properties? Estimate the approximate electronegativity of a pure element that is very dense, lustrous, and malleable.

13. Of the elements Al, Mg, O_2, Ti, I_2, and H_2, which, if any, would you expect to be a good reductant? Explain your reasoning.

14. Of the elements Zn, B, Li, Se, Co, and Br_2, which if any, would you expect to be a good oxidant? Explain your reasoning.

15. Determine whether each species is a good oxidant, a good reductant, or neither.

    1. Ba
    2. Mo
    3. Al
    4. Ni
    5. O_2
    6. Xe

16. Determine whether each species is a good oxidant, a good reductant, or neither.

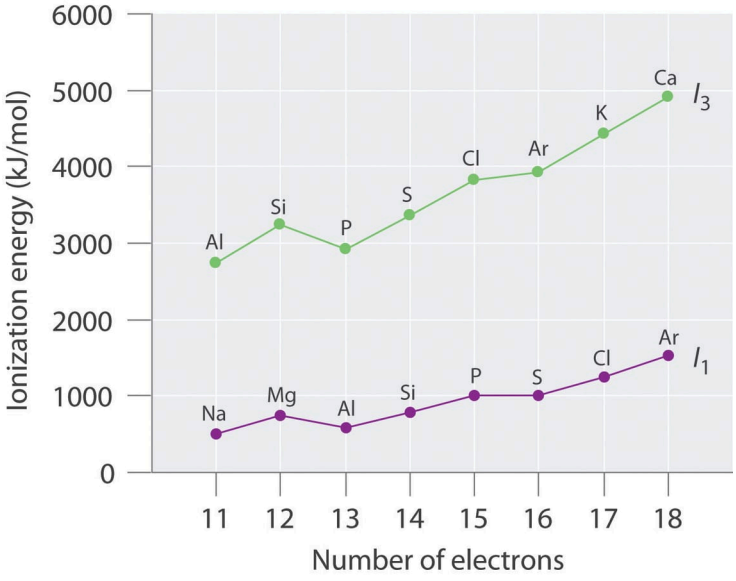
    1. Ir
    2. Cs
    3. Be
    4. B
    5. N
    6. Po
    7. Ne

17. Of the species I_2, O^-, Zn, Sn^{2+}, and K^+, choose which you would expect to be a good oxidant. Then justify your answer.

18. Based on the valence electron configuration of the noble gases, would you expect them to have positive or negative electron affinities? What does this imply about their most likely oxidation states? their reactivity?

Numerical Answers

1.



The general features of both plots are roughly the same, with a small peak at 12 electrons and an essentially level region from 15–16 electrons. The slope of the I_3 plot is about twice as large as the slope of the I_1 plot, however, because the I_3 values correspond to removing an electron from an ion with a +2 charge rather than a neutral atom. The greater charge increases the effect of the steady rise in effective nuclear charge across the row.

2.

3. Electron configurations: Mg, $1s^2 2s^2 2p^6 3s^2$; Al, $1s^2 2s^2 2p^6 3s^2 3p^1$; Si, $1s^2 2s^2 2p^6 3s^2 3p^2$; First ionization energies increase across the row due to a steady increase in effective nuclear charge; thus, Si has the highest first ionization energy. The third ionization energy corresponds to removal of a 3s electron for Al and Si, but for Mg it involves removing a 2*p* electron from a filled inner shell; consequently, the third ionization energy of Mg is the highest.

4.

5.

6.

7. 1. Bi > As > N
   2. F > O >> Ar
   3. Rb > Cs > Ba

8.

9. $Hg^{2+} > H^+ > O^- > N^{2-}$; Hg^{2+} has the highest positive charge plus a relatively low energy vacant set of orbitals (the 6*p* subshell) to accommodate an added electron, giving it the greatest electron affinity; N^{2-} has a greater negative charge than O^-, so electron–electron repulsions will cause its electron affinity to be even lower (more negative) than that of O^-.

10.

11. insulators: S, O, C (diamond), P; conductors: Ba, Fe, Al, C (graphite), Be, Sc, W, Na, Rb; Te and B are semimetals and semiconductors.

12.

13. Mg, Al, Ti, and H_2

14.

15. 1. reductant
   2. neither
   3. reductant

4. reductant
5. oxidant
6. neither

16.

17. I_2 is the best oxidant, with a moderately strong tendency to accept an electron to form the I^- ion, with a closed shell electron configuration. O^- would probably also be an oxidant, with a tendency to add an electron to form salts containing the oxide ion, O^{2-}. Zn and Sn^{2+} are all reductants, while K^+ has no tendency to act as an oxidant or a reductant.

7.5: Electron Affinities

see above question to tease out

7.6: Metals, Nonmetals, and Metalloids

7.7: Group Trends fo the Active Metals

7.8: Group Trends for Selected Nonmetals

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7.S: Periodic Properties of the Elements (Summary)

7.1: Development of the Periodic Table

- 1869: Dmitri Mendeleev (Russia) and Lothar Meyer (Germany) publish nearly identical schemes for classifying the elements
- Both had arranged the elements in order of increasing atomic weights
- Mendeleev predicted the existence and properties of Germanium (Ge) and Gallium (Ga). When they were discovered, their properties were found to closely match those predicted by Mendeleev
- 1913: Henry Moseley discovers concept of atomic numbers. Observed that frequencies of Xrays were different for each element. Was able to arrange these frequencies in order by assigning each element a unique whole number, which he called the *atomic number*

7.2: Effective Nuclear Charge

- Orbitals with the same value of *n* are referred to as a *shell*
- When looking at a radial electrondensity graph, the maxima (peaks) designate the areas with the higher probabilities of finding electrons
- The 1s shell in Argon is closer to the nucleus than that of Helium. This is because both 1s shells are the only ones not shielded from the nucleus by other electrons. However, since Argon has a stronger nuclear charge, it can attract its electrons more easily
- radial electron density – probability of finding the electron at a particular distance from the nucleus
- as nuclear charge increases, 1s shells pulled closer to nucleus

7.3: Sizes of Atoms and Ions

Atomic radius: radius of an atom of a given element

1. Within each group, the atomic radius tends to increase going from top to bottom
2. Within each period, the atomic radius tends to decrease moving left to right

Two factors determine the size of the outermost orbital

1. Its principal quantum number (as it increases, the size of the orbital increases)
2. The effective nuclear charge (reduces the size of the orbital by pulling electrons closer)

Atomic Sizes

- atomic radius – estimation of radius of atoms
- estimate by assuming that atoms are spheres that touch each other
- atomic radius increases down a group, decrease down row
- atomic radius affected by principal quantum number and effective nuclear charge
- increase principal quantum number, increases size of orbital
- increase effective nuclear charge, reduces size or orbital

7.4: Ionization Energy

Ionization energy: energy required to remove an electron from a gaseous atom when the atom is in its ground state.

- first ionization energy – energy needed to remove the first electron
- second ionization energy – energy needed to remove second electron
- the greater ionization energy, harder it is to remove electrons
- The *first* ionization energy, I_1, is the energy needed to remove the first electron. The *second* ionization energy, I_2, removes the second electron, and so on. The HIGHER the ionization energy, the MORE DIFFICULT it is to remove an electron.

Every element exhibits a large increase in ionization energy when electrons are removed from its noblegas core. The inner electrons are too tightly bound to the nucleus to be lost from the atom or even shared with another atom

$$I_1 < I_2 < I_3$$

- Positive nuclear charge remains same, number electrons decreases -> effective nuclear charge increases
- Greater effective nuclear charge, greater energy required to remove electron
- Sharp increase in ionization energy when inner-shell electron removed
- Only outer most electrons involved in sharing and transfer of electrons in bonding and reactions

Periodic Trends in Ionization Energies

1. Within each period, I_1 generally increases with increasing atomic number. The alkali metals show the lowest ionization energy in each row, and the noble gases the highest
2. Within each group, ionization energy generally decreases with increasing atomic number.

- Energy needed to remove electrons from outer shell depends on nuclear charge and average distance between of the electron from the nucleus
- As we move across a period, there is both an increase in effective nuclear charge and a decrease in atomic radius, causing the ionization energy to increase
- As we move down a column, the atomic radius increases, while the effective charge remains essentially constant. Thus, the attraction between the nucleus and the electron decreases in this direction, causing the ionization energy to decrease.

7.5: Electron Affinities

- **Electron affinity**: energy change that occurs when an electron is added to a gaseous atom or ion
- For most neutral atoms and for all positively charged ions, energy is released when an electron is added
- The greater the attraction between the species and the added electron, the more exothermic the process
- On the other hand, adding an electron to anions and to some atoms makes them unstable.
- The general trend for electron affinity is to become increasingly negative (stronger binding of electrons) as we move across each period toward the halogens. The halogens have the most negative electron affinities since they are one electron short of noblegas configuration
- Electron affinities do not change greatly as we go down a group

7.6: Metals, Nonmetals, and Metalloids

Metallic Elements and Nonmetallic Elements

Metallic elements	Nonmetallic elements
Distinguishing luster	Nonlustrous; various colors
Malleable and ductile as solids	Solids are usually brittle; may be hard or soft
Good thermal and electrical conductivity	Poor conductors of heat and electricity
Most metallic oxides are basic, ionic solids	Most nonmetallic oxides are molecular, acidic compounds
Exist in aqueous solution mainly as cations	Exist in aqueous solution mainly as anions or oxyanions

Metals

- See properties above. All are solids at room temperature except mercury, which is a liquid.
- Metals tend to have low ionization energies and are consequently oxidized (lose electrons) when they undergo chemical reaction.
- Compounds of metals with nonmetals tend to be ionic substances
- Most metals are **basic oxides** (oxide that either reacts with water to form a base or reacts with an acid to form a salt and water)

Nonmetals

- Generally have lower melting points than those of metals.
- Seven nonmetals exist as diatomic molecules under ordinary conditions (H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2). Bromine is liquid; Iodine is a volatile solid, the rest are gases. The remaining nonmetals are solids.
- Nonmetals, in reacting with metals, tend to gain electrons and become anions
- Compound composed entirely of nonmetals are molecular substances
- Most nonmetals are **acidic oxides** (oxide that forms acid when added to water; soluble nonmetal oxides are acidic oxides)

Metalloids

- Have properties intermediate between those of metals and nonmetals. May have some metallic properties but lack others.
- Several metalloids are electrical semiconductors

Trends in Metallic and Nonmetallic Character

Metallic character: the extent to which an element exhibits the physical and chemical properties characteristic of metals, for example, luster, malleability, ductility, and good thermal and electrical conductivity.

1. Metallic character is strongest for the elements in the leftmost part of the periodic table and tends to decrease as we move to the right in any period
2. Within any group of representative elements, the metallic character increases progressively from top to bottom

7.7: Group Trends for the Active Metals

Group 1: The Alkali Metals

- Metallic properties; silvery, metallic luster, high thermal and electrical conductivity
- Low densities and melting points; increasing atomic radius and decreasing ionization energy as we move down the family
- Lowest I_1 values of the elements, which reflects the ease with which their outer electrons can be removed. This makes the alkali metals very reactive, readily losing one electron.
- In the hydrides of the alkali metals (LiH, NaH, and so forth), hydrogen is present as H, called the **hydride ion**.
- The alkali metals react vigorously with water, producing hydrogen gas and solutions of alkali metal hydroxides (very exothermic).

Group 2: The Alkaline Earth Metals

- Solids, typical metallic properties, denser and harder than alkali metals (also melt at higher temperatures)
- Less reactive than alkali metals (have slightly higher ionization energy)
- Ease with which the elements lose their electrons increases as we move down the family

7.8: Group Trends for Selected Nonmetals

Hydrogen

- Hydrogen is a nonmetal, which occurs as a diatomic gas under normal conditions
- Its ionization energy is considerably higher (due to lack of shielding, and thus higher Z_{eff}) thatn the metals and is more like the nonmetals
- Hydrogen generally reacts with other nonmetals to form molecular compounds (typically highly exothermic)
- Hydrogen reacts with active metals to form metal hydrides that contain the H hydride ion
- Hydrogen can also lose an electron to yield the aqueous H^+ ion

Group 16: The Oxygen Family

- As we proceed down group 6A, the increase in metallic character is clearly evident
- **Allotropes**: different forms of the same element in the same state (ie: O_2 and O_3)
- Oxygen has a great tendency to attract electrons from other elements ("oxidize" them)
- Oxygen in combination with metals is almost always present as the oxide, O^2 ion, which has noblegas configuration and is

particularly stable
- Sulfur is the second most important element in the 6A group. It also exists in several allotropic, the most common and stable being S_8.
- Sulfur also has a great tendency to gain electrons from other elements to form sulfides
- Because Sulfur is below Oxygen, its tendency to form sulfide anions is not is not as great as that of Oxygen to form oxide ions

Group 17: The Halogens

- All halogens are typical nonmetals. Their melting and boiling points increase with increasing atomic numbers
- Fluorine and Chlorine are gases at room temperature, Bromine is a liquid, and Iodine is a solid
- The halogens have among the most negative electron affinities; they have a great tendency to gain electrons.
- Fluorine and Chlorine are the most reactive. Fluorine removes electrons from almost any substance, even water, and usually very exothermically.
- Halogens react with most metals to form ionic halides and with Hydrogen to form gaseous hydrogen halides.

Group 18: The Noble Gases

- All noble gases are monoatomic (single atom)
- All have large first ionization energies, with a decrease as we go down the group
- Until the early 1960's, they were called *inert gases* because they were thought to be incapable of forming chemical compounds.
- Only noblegas compounds known today are: XeF_2, XeF_4, XeF_6, and KrF_2

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8: BASIC CONCEPTS OF CHEMICAL BONDING

We described the relationship between the chemical properties and reactivity of an element and its position in the periodic table. In this chapter and the following chapter, we describe the interactions that hold atoms together in chemical substances, and we examine the factors that determine how the atoms of a substance are arranged in space. Our goal is to understand how the properties of the component atoms in a chemical compound determine the structure and reactivity of the compound. The properties described previously were properties of isolated atoms, yet most of the substances in our world consist of atoms held together in molecules, ionic compounds, or metallic solids. The properties of these substances depend on not only the characteristics of the component atoms but also how those atoms are bonded to one another.

What you learn in this chapter about chemical bonding and molecular structure will help you understand how different substances with the same atoms can have vastly different physical and chemical properties. For example, oxygen gas (O_2) is essential for life, yet ozone (O_3) is toxic to cells, although as you learned previously, ozone in the upper atmosphere shields us from harmful ultraviolet light. Moreover, you saw that diamond is a hard, transparent solid that is a gemstone; graphite is a soft, black solid that is a lubricant; and fullerenes are molecular species with carbon cage structures—yet all of these are composed of carbon. As you learn about bonding, you will also discover why, although carbon and silicon both have ns^2np^2 valence electron configurations and form dioxides, CO_2 is normally a gas that condenses into the volatile molecular solid known as dry ice, whereas SiO_2 is a nonvolatile solid with a network structure that can take several forms, including beach sand and quartz crystals.

8.1: Chemical Bonds, Lewis Symbols, and the Octet Rule

8.2: Ionic Bonding

8.3: Covalent Bonding

8.4: Bond Polarity and Electronegativity

8.5: Drawing Lewis Structures

8.6: Resonance Structures

8.7: Exceptions to the Octet Rule

8.8: Strength of Covalent Bonds

8.E: Basic Concepts of Chemical Bonding (Exercises)

8.S: Basic Concepts of Chemical Bonding (Summary)

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8.1: Chemical Bonds, Lewis Symbols, and the Octet Rule

Learning Objectives

- To use Lewis electron dot symbols to predict the number of bonds an element will form.

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond wil be discussed and the general properties found in typical substances in which the bond type occurs

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involves a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involves one nonmetallic element with another
3. Metallic bonds These bonds are found in solid metals (copper, iron, aluminum) with each metal bonded to several neighboring groups and bonding electrons free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

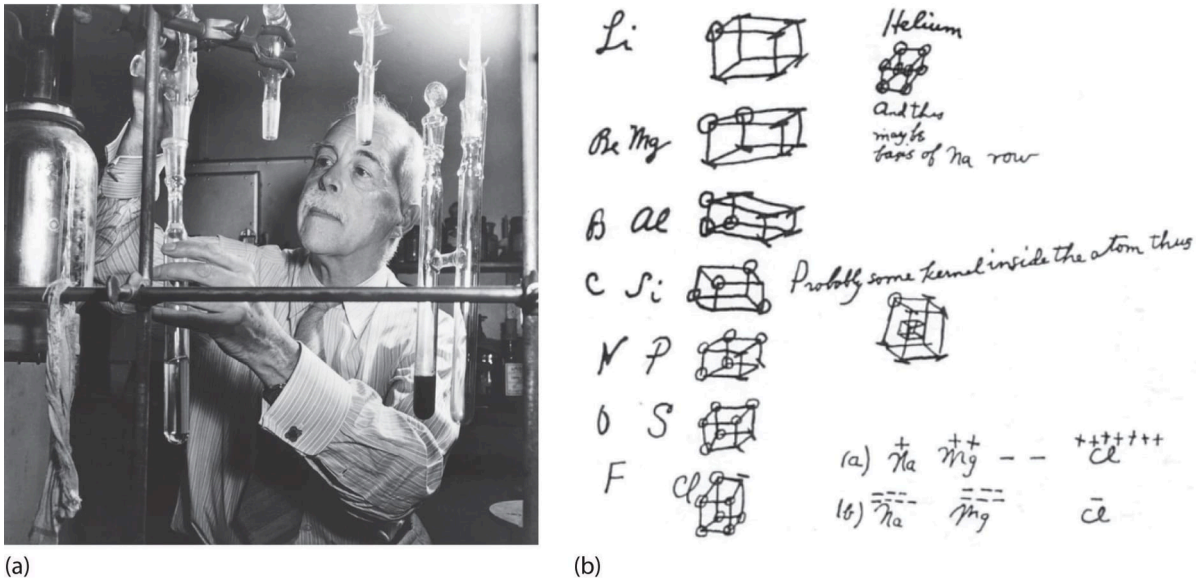


Figure 8.1.1: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Symbols

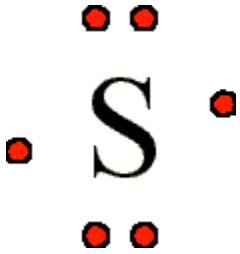
At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots

that represent its valence electrons.

Lewis Dot symbols:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is $[Ne]3s^2 3p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration $[He]2s^2 2p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:

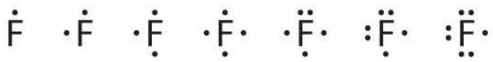


Figure 8.1.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 8.1.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Element	Electron config.	Electron dot symbol
Li	$[He]2s^1$	Li•
Be	$[He]2s^2$	•Be•
B	$[He]2s^22p^1$	•B•
C	$[He]2s^22p^2$	•C•
N	$[He]2s^22p^3$	•N:
O	$[He]2s^22p^4$	:O:
F	$[He]2s^22p^5$	:F:
Ne	$[He]2s^22p^6$	:Ne:

Figure 8.1.2: Lewis Dot Symbols for the Elements in Period 2

L i has one dot on the right, B e has one dot on the left and right, B has one dot on the left, right, and above. C has one dot above, below, on the left and on the right. N has one dot above, below, on the left and two dots on the right. O has two dots on the left and right and one dot above and below. F has two dots above, on the left, on the right and on dot below. N e has two dots above, below, on the right, and on the left.

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The Octet Rule

In 1904, Richard Abegg formulated what is now known as *Abegg's rule*, which states that the difference between the maximum positive and negative valences of an element is frequently eight. This rule was used later in 1916 when Gilbert N. Lewis formulated the "octet rule" in his cubical atom theory. The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. Atoms will react to get in the most stable state possible. A complete octet is very stable because all orbitals will be full. Atoms with greater stability have less energy, so a reaction that increases the stability of the atoms will release energy in the form of heat or light ;reactions that decrease stability must absorb energy, getting colder.

When discussing the octet rule, we do not consider *d* or *f* electrons. Only the s and p electrons are involved in the octet rule, making it a useful rule for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6.

Definition: Octet Rule

A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

1. Normally two electrons pairs up and forms a bond, e.g., H_2

2. For most atoms there will be a maximum of eight electrons in the valence shell (octet structure), e.g., $\mathrm{CH_4}$

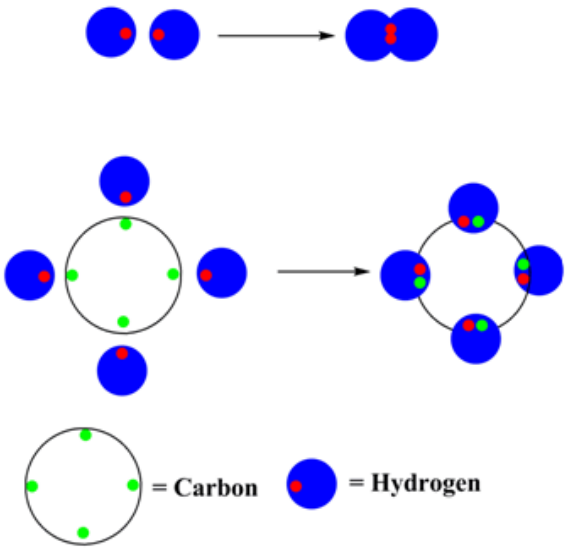


Figure 1: Bonding in H_2 and methane (CH_4)

A hydrogen bonds with each of the four valence electrons of a carbon meaning that four hydrogens can bond with one carbon.

The other tendency of atoms is to maintain a neutral charge. Only the noble gases (the elements on the right-most column of the periodic table) have zero charge with filled valence octets. All of the other elements have a charge when they have eight electrons all to themselves. The result of these two guiding principles is the explanation for much of the reactivity and bonding that is observed within atoms: atoms seek to share electrons in a way that minimizes charge while fulfilling an octet in the valence shell.

The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

Example 8.1.1: Salt

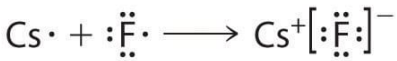
The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why?

Solution

Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium has one valence electron, so giving it up would result in the same electron configuration as neon. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon when it gains an electron.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gasses, with a full valence shell. However, their charges would be much higher. It would be Na^{7-} and Cl^{7+}, which is much less stable than Na^+ and Cl^-. Atoms are more stable when they have no charge, or a small charge.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

> Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe elsewhere. These include molecules in which one or more atoms contain fewer or more than eight electrons.

Summary

Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds. One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

Contributors and Attributions

- Mike Blaber (Florida State University)

- Wikipedia
- National Programme on Technology Enhanced Learning (India)

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8.2: Ionic Bonding

Learning Objectives

- To describe the characteristics of ionic bonding.
- To quantitatively describe the energetic factors involved in the formation of an ionic bond.

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge. Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged. **Ionic bonding** is the attraction between positively- and negatively-charged ions. These oppositely charged ions attract each other to form ionic networks (or **lattices**). Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

Generating Ionic Bonds

Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding.

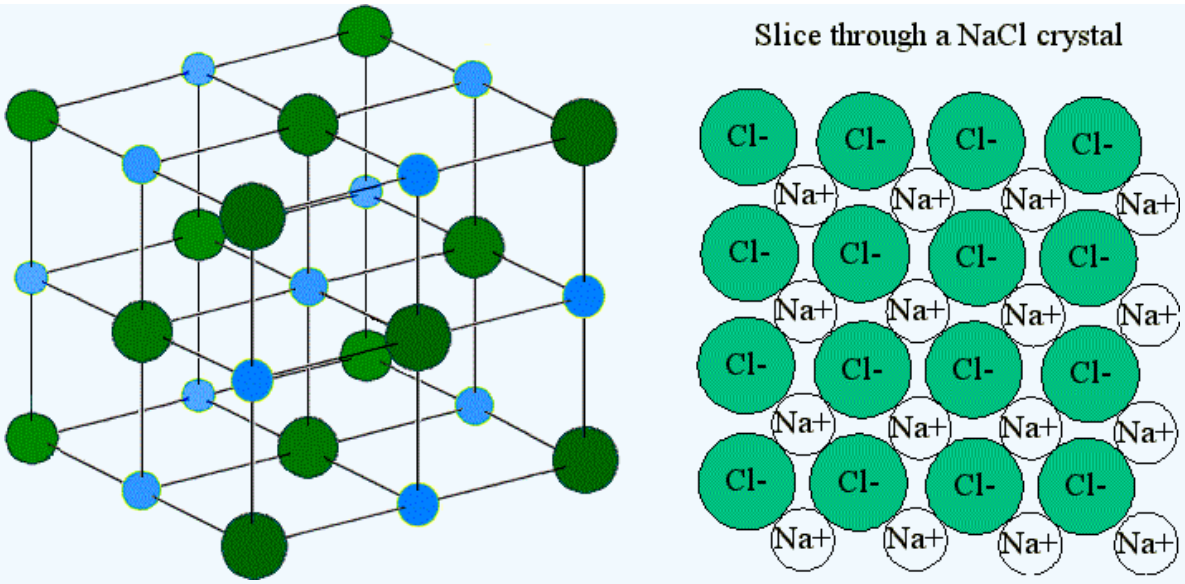
In the overall ionic compound, positive and negative charges must be balanced, because electrons cannot be created or destroyed, only transferred. Thus, the total number of electrons lost by the cationic species must equal the total number of electrons gained by the anionic species.

Example 8.2.1: Sodium Chloride

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is NaCl.

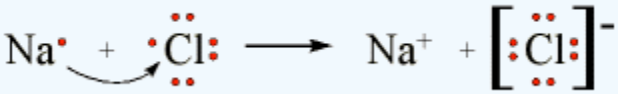
$$2\,\mathrm{Na\,(s)} + \mathrm{Cl}\ 2\,\mathrm{(g)} \ \rightarrow 2\,\mathrm{NaCl\,(s)}$$

These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):



NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattes. Images used with permission from Wikipedia and Mike Blaber.

The chlorine has a high affinity for electrons, and the sodium has a low ionization energy. Thus the chlorine gains an electron from the sodium atom. This can be represented using ewis dot symbols (here we will consider one chlorine atom, rather than Cl_2):



Chlorine becomes more negative when it takes the one valence electron from sodium when it makes an octet.

The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an **octet** of electrons in its valence shell:

- Na^{+}: $2s^2 2p^6$
- Cl^{-}: $3s^2 3p^6$

Energetics of Ionic Bond Formation

Ionic bonds are formed when positively and negatively charged ions are held together by electrostatic forces. Consider a single pair of ions, one cation and one anion. How strong will the force of their attraction be? According to **Coulomb's Law**, the energy of the electrostatic attraction (E) between two charged particles is proportional to the magnitude of the charges and inversely proportional to the internuclear distance between the particles (r):

$$E \propto \frac{Q_1 Q_2}{r} \tag{8.2.1}$$

$$E = k\frac{Q_1 Q_2}{r} \tag{8.2.2}$$

where each ion's charge is represented by the symbol Q. The proportionality constant *k* is equal to 2.31×10^{-28} J·m. This value of *k* includes the charge of a single electron (1.6022×10^{-19} C) for each ion. The equation can also be written using the charge of each ion, expressed in coulombs (C), incorporated in the constant. In this case, the proportionality constant, *k*, equals 8.999×109 J·m/C^2. In the example given, $Q_1 = +1(1.6022 \times 10^{-19}$ C) and $Q_2 = -1(1.6022 \times 10^{-19}$ C). If Q_1 and Q_2 have opposite signs (as

in NaCl, for example, where Q_1 is +1 for Na^+ and Q_2 is –1 for Cl^-), then E is negative, which means that energy is *released* when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair.

Energy is always released when a bond is formed and correspondingly, it always requires energy to break a bond.

As shown by the green curve in the lower half of Figure 8.2.1, the maximum energy would be released when the ions are infinitely close to each other, at r = 0. Because ions occupy space and have a structure with the positive nucleus being surrounded by electrons, however, they cannot be infinitely close together. At very short distances, repulsive electron–electron interactions between electrons on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the red curve in the upper half of Figure 8.2.1. The total energy of the system is a balance between the attractive and repulsive interactions. The purple curve in Figure 8.2.1 shows that the total energy of the system reaches a minimum at r_0, the point where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured **bond distance**.

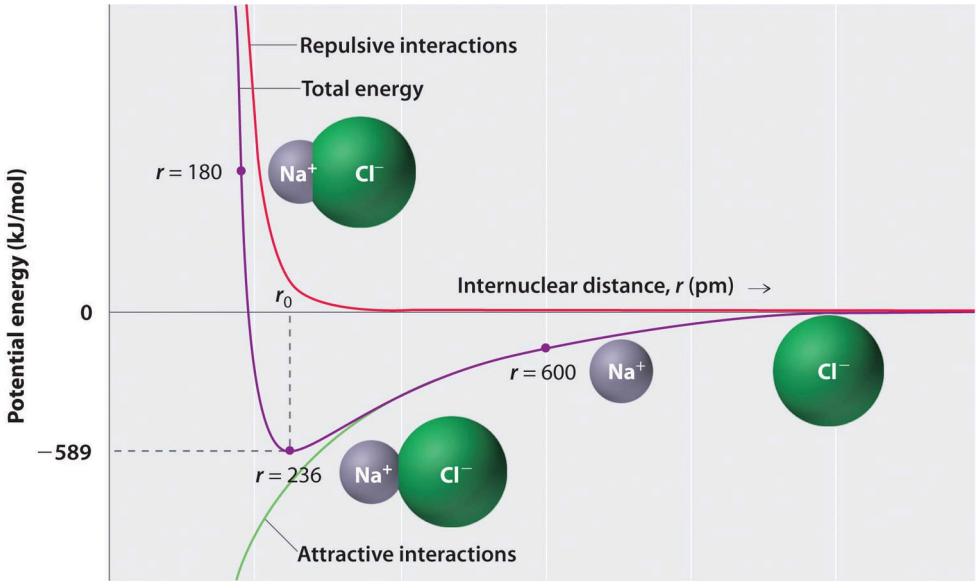


Figure 8.2.1: A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na^+ Ion and a Gaseous Cl^- Ion. The energy of the system reaches a minimum at a particular distance (r_0) when the attractive and repulsive interactions are balanced.

Consider the energy released when a gaseous Na^+ ion and a gaseous Cl^- ion are brought together from r = ∞ to $r = r_0$. Given that the observed gas-phase internuclear distance is 236 pm, the energy change associated with the formation of an ion pair from an $Na^+_{(g)}$ ion and a $Cl^-_{(g)}$ ion is as follows:

$$\begin{aligned} E &= k\frac{Q_1Q_2}{r_0} \\ &= (2.31 \times 10^{-28}\text{J} \cdot \cancel{\text{m}}) \left(\frac{(+1)(-1)}{236\ \cancel{\text{pm}} \times 10^{-12}\ \cancel{\text{m/pm}}} \right) \\ &= -9.79 \times 10^{-19}\ J/ion\ pair \end{aligned}$$

The negative value indicates that energy is released. Our convention is that if a chemical process provides energy to the outside world, the energy change is negative. If it requires energy, the energy change is positive. To calculate the energy change in the formation of a mole of NaCl pairs, we need to multiply the energy per ion pair by Avogadro's number:

$$E = \left(-9.79 \times 10^{-19}\ J/\cancel{ion pair}\right)\left(6.022 \times 10^{23}\ \cancel{ion\ pair}/mol\right) = -589\ kJ/mol \tag{8.2.3}$$

This is the energy released when 1 mol of gaseous ion pairs is formed, *not* when 1 mol of positive and negative ions condenses to form a crystalline lattice. Because of long-range interactions in the lattice structure, this energy does not correspond directly to the **lattice energy** of the crystalline solid. However, the large negative value indicates that bringing positive and negative ions together is energetically very favorable, whether an ion pair or a crystalline lattice is formed.

We summarize the important points about ionic bonding:

- At r_0, the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from $r = \infty$ to $r = r_0$, the energy of the system is lowered (energy is released).
- Because of the low potential energy at r_0, energy must be added to the system to separate the ions. The amount of energy needed is the bond energy.
- The energy of the system reaches a minimum at a particular internuclear distance (the bond distance).

Example 8.2.2: LiF

Calculate the amount of energy released when 1 mol of gaseous Li^+F^- ion pairs is formed from the separated ions. The observed internuclear distance in the gas phase is 156 pm.

Given: cation and anion, amount, and internuclear distance

Asked for: energy released from formation of gaseous ion pairs

Strategy:

Substitute the appropriate values into Equation 8.2.2 to obtain the energy released in the formation of a single ion pair and then multiply this value by Avogadro's number to obtain the energy released per mole.

Solution:

Inserting the values for Li^+F^- into Equation 8.2.2 (where $Q_1 = +1$, $Q_2 = -1$, and $r = 156$ pm), we find that the energy associated with the formation of a single pair of Li^+F^- ions is

$$\begin{aligned} E &= k\frac{Q_1Q_2}{r_0} \\ &= \left(2.31 \times 10^{-28} J \cdot \cancel{m}\right)\left(\frac{(+1)(-1)}{156\ pm \times 10^{-12}\ \cancel{m/pm}}\right) \\ &= -1.48 \times 10^{-18} \end{aligned}$$

Then the energy released per mole of Li^+F^- ion pairs is

$$\begin{aligned} E = &\left(-1.48 \times 10^{-18} J/\cancel{\text{ion pair}}\right)\left(6.022 \times 10^{23}\ \cancel{\text{ion pair}}/mol\right) \\ &-891\ kJ/mol \end{aligned}$$

Because Li^+ and F^- are smaller than Na^+ and Cl^- (see Section 7.3), the internuclear distance in LiF is shorter than in NaCl. Consequently, in accordance with Equation 8.2.2, much more energy is released when 1 mol of gaseous Li^+F^- ion pairs is formed (–891 kJ/mol) than when 1 mol of gaseous Na^+Cl^- ion pairs is formed (–589 kJ/mol).

Exercise 8.2.2: Magnesium oxide

Calculate the amount of energy released when 1 mol of gaseous MgO ion pairs is formed from the separated ions. The internuclear distance in the gas phase is 175 pm.

Answer available at the end of this section.

Electron Configuration of Ions

How does the energy released in lattice formation compare to the energy required to strip away a second electron from the Na^+ ion? Since the Na^+ ion has a noble gas electron configuration, stripping away the next electron from this stable arrangement would require more energy than what is released during lattice formation (Sodium I_2 = 4,560 kJ/mol). Thus, sodium is present in ionic compounds as Na^+ and not Na^{2+}. Likewise, adding an electron to fill a valence shell (and achieve noble gas electron configuration) is exothermic or only slightly endothermic. To add an additional electron into a ***new*** subshell requires tremendous energy - more than the lattice energy. Thus, we find Cl^- in ionic compounds, but not Cl^{2-}.

Table 8.2.1: Lattice energies range from around 700 kJ/mol to 4000 kJ/mol:

Compound	Lattice Energy (kJ/mol)
LiF	1024
LiI	744
NaF	911
NaCl	788
NaI	693
KF	815
KBr	682
KI	641
MgF_2	2910
$SrCl_2$	2130
MgO	3938

This amount of energy can compensate for values as large as I_3 for valence electrons (i.e. can strip away up to 3 valence electrons). Because most transition metals would require the removal of more than 3 electrons to attain a noble gas core, they are not found in ionic compounds with a noble gas core. A transition metal always loses electrons first from the higher 's' subshell, before losing from the underlying 'd' subshell. (The remaining electrons in the unfilled d subshell are the reason for the bright colors observed in many transition metal compounds!) For example, iron ions will **not** form a noble gas core:

- Fe: $[Ar]4s^23d^6$
- Fe^{2+}: $[Ar]\ 3d^6$
- Fe^{3+}: $[Ar]\ 3d^5$

Some metal ions can form a pseudo noble gas core (and be colorless), for example:

- Ag: $[Kr]5s^14d^{10}$ Ag^+ $[Kr]4d^{10}$ Compound: AgCl
- Cd: $[Kr]5s^24d^{10}$ Cd^{2+} $[Kr]4d^{10}$ Compound: CdS

The valence electrons do not adhere to the "octet rule" in this case (a limitation of the usefulness of this rule). Note: The silver and cadmium atoms lost the 5s electrons in achieving the ionic state.

> When a positive ion is formed from an atom, electrons are **always** lost first from the subshell with the largest principle quantum number

Polyatomic Ions

Not all ionic compounds are formed from only two elements. Many **polyatomic ions** exist, in which two or more atoms are bound together by covalent bonds. They form a stable grouping which carries a charge (positive or negative). The group of atoms as a

whole acts as a charged species in forming an ionic compound with an oppositely charged ion. Polyatomic ions may be either positive or negative, for example:

- NH_4^+ (ammonium) = cation
- SO_4^{2-} (sulfate) = anion

The principles of ionic bonding with polyatomic ions are the same as those with monatomic ions. Oppositely charged ions come together to form a crystalline lattice, releasing a lattice energy. Based on the shapes and charges of the polyatomic ions, these compounds may form crystalline lattices with interesting and complex structures.

Summary

The amount of energy needed to separate a gaseous ion pair is its bond energy. The formation of ionic compounds are usually ***extremely exothermic***. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

Contributors and Attributions

- Wikibooks [en.wikibooks.org]
- Mike Blaber (Florida State University)
- Modified by Joshua Halpern (Howard University)

Answers

Exercise 8.2.2: Magnesium oxide

−3180 kJ/mol = -3.18×10^3 kJ/mol

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8.3: Covalent Bonding

Learning Objectives

- To understand the relationship between bond order, bond length, and bond energy.

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds. The general properties of Ionic substances are:

- usually brittle
- high melting point
- organized into an ordered lattice of atoms, which can be cleaved along a smooth line

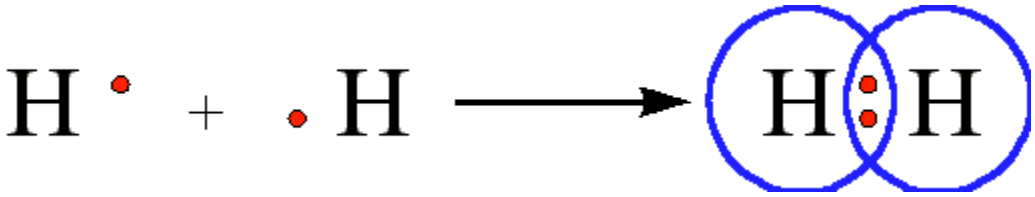
However, the vast majority of chemical substances are ***not ionic*** in nature. G.N. Lewis reasoned that an atom might attain a noble gas electron configuration by ***sharing*** electrons.

> A chemical bond formed by sharing a pair of electrons is called a covalent bond

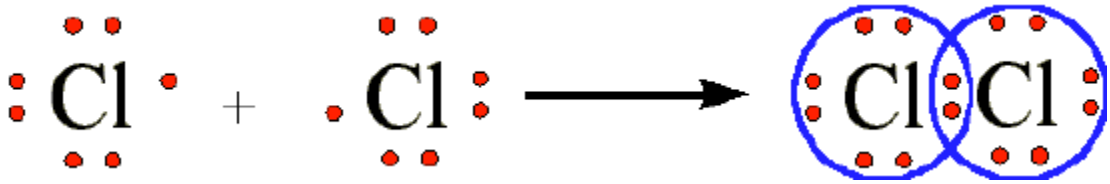
Lewis Structures

Lewis structures (also known as Lewis dot diagrams, electron dot diagrams, Lewis dot formulas, Lewis dot structures, and electron dot structures) are diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule. Lewis structures show each atom and its position in the structure of the molecule using its chemical symbol. Lines are drawn between atoms that are bonded to one another (pairs of dots can be used instead of lines). Excess electrons that form lone pairs are represented as pairs of dots, and are placed next to the atoms.

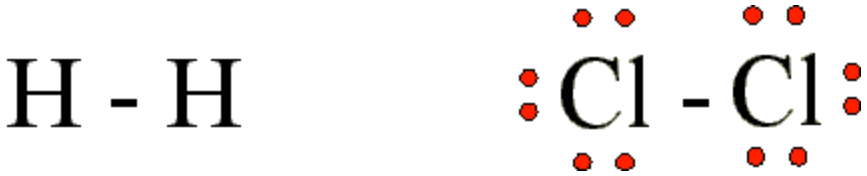
The diatomic hydrogen molecule (H_2) is the simplest model of a covalent bond, and is represented in Lewis structures as:



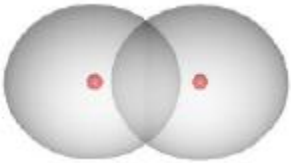
The ***shared pair*** of electrons provides ***each*** hydrogen atom with two electrons in its valence shell (the 1s) orbital. In a sense, each hydrogen atoms has the electron configuration of the noble gas helium When two chlorine atoms covalently bond to form Cl_2, the following sharing of electrons occurs:



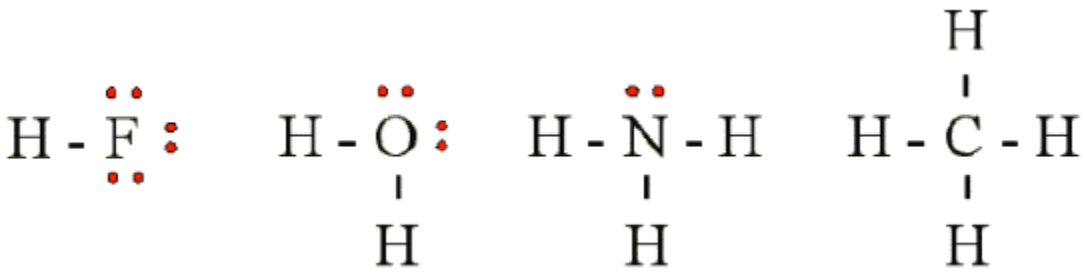
Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon. In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:



The shared electrons are not located in a fixed position between the nuclei. In the case of the H_2 compound, the electron density is concentrated between the two nuclei:



The two atoms are bound into the H_2 molecule mainly due to the attraction of the positively charged nuclei for the negatively charged electron cloud located between them. Examples of hydride compounds of the above elements (covalent bonds with hydrogen:



Multiple bonds

The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them:

- Two electron pairs shared a ***double bond***
- Three electron pairs shared a ***triple bond***



If two electron pairs are shared then two lines are drawn. If three electron pairs are shared then three lines are drawn

Because each nitrogen contains 5 valence electrons, they need to share 3 pairs to each achieve a valence octet. N_2 is fairly inert, due to the strong triple bond between the two nitrogen atoms and the N - N bond distance in N_2 is 1.10 Å (fairly short). From a study of various Nitrogen containing compounds bond distance as a function of bond type can be summarized as follows:

- $\mathrm{N{-}N}$: 1.47Å
- $\mathrm{N{=}N}$: 1.24Å
- $\mathrm{N:{\equiv}N}$:1.10Å

For the nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number:

nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number

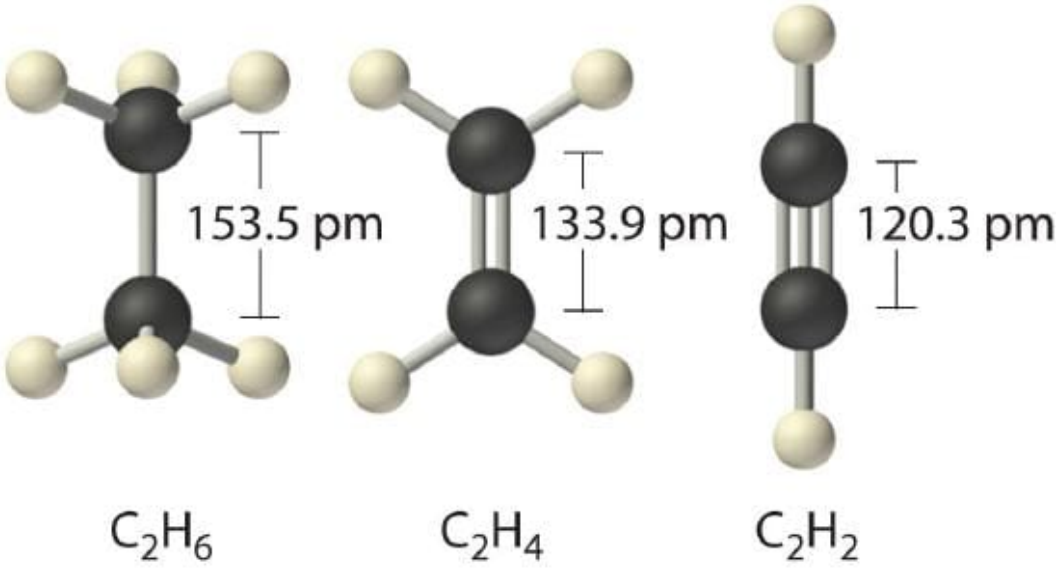
Element	Group	Valence electrons	Bonds needed to form valence octet
aF	17	7	1
O	16	6	2
N	15	5	3
C	14	4	4

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Thus, the Lewis bonds successfully describe the covalent interactions between various nonmetal elements. When we draw Lewis structures, we place one, two, or three pairs of electrons between adjacent atoms. In the Lewis bonding model, the number of electron pairs that hold two atoms together is called the bond order. For a single bond, such as the C–C bond in $H_3C–CH_3$, the bond order is one. For a double bond (such as $H_2C=CH_2$), the bond order is two. For a triple bond, such as HC≡CH, the bond order is three.



When analogous bonds in similar compounds are compared, bond length decreases as bond order increases. The bond length data in Table 8.3.1, for example, show that the C–C distance in $H_3C–CH_3$ (153.5 pm) is longer than the distance in $H_2C=CH_2$ (133.9 pm), which in turn is longer than that in HC≡CH (120.3 pm). Additionally, as noted in Section 8.5, molecules or ions whose bonding must be described using resonance structures usually have bond distances that are intermediate between those of single and double bonds, as we demonstrated with the C–C distances in benzene. The relationship between bond length and bond order is not linear, however. A double bond is not half as long as a single bond, and the length of a C=C bond is not the average of the lengths of C≡C and C–C bonds. Nevertheless, as bond orders increase, bond lengths generally decrease.

Table 8.3.1: Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K

Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)
$H_3C–CH_3$	1	153.5	376	$H_3C–NH_2$	1	147.1	331
$H_2C=CH_2$	2	133.9	728	$H_2C=NH$	2	127.3	644
HC≡CH	3	120.3	965	HC≡N	3	115.3	937
$H_2N–NH_2$	1	144.9	275.3	$H_3C–OH$	1	142.5	377
HN=NH	2	125.2	456	$H_2C=O$	2	120.8	732
N≡N	3	109.8	945.3	O=C=O	2	116.0	799
HO–OH	1	147.5	213	C≡O	3	112.8	1076.5
O=O	2	120.7	498.4				

Sources: Data from *CRC Handbook of Chemistry and Physics* (2004); *Lange's Handbook of Chemistry* (2005); CCCBDB [cccbdb.nist.gov].

As a general rule, the distance between bonded atoms decreases as the number of shared electron pairs increases

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The Relationship between Bond Order & Bond Energy

As shown in Table 8.3.1, triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however.

Table 8.3.1: Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										Multiple Bonds	
H–H	432	C–C	346	N–N	≈167	O–O	≈142	F–F	155	C=C	602
H–C	411	C–Si	318	N–O	201	O–F	190	F–Cl	249	C≡C	835
H–Si	318	C–N	305	N–F	283	O–Cl	218	F–Br	249	C=N	615
H–N	386	C–O	358	N–Cl	313	O–Br	201	F–I	278	C≡N	887
H–P	≈322	C–S	272	N–Br	243	O–I	201	Cl–Cl	240	C=O	749
H–O	459	C–F	485	P–P	201	S–S	226	Cl–Br	216	C≡O	1072
H–S	363	C–Cl	327			S–F	284	Cl–I	208	N=N	418
H–F	565	C–Br	285			S–Cl	255	Br–Br	190	N≡N	942

Single Bonds									Multiple Bonds	
H–Cl	428	C–I	213		S–Br	218	Br–I	175	N=O	607
H–Br	362	Si–Si	222				I–I	149	O=O	494
H–I	295	Si–O	452						S=O	532
Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry*, 4th ed. (1993).										

Table 8.3.2 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H–F bond is stronger than an H–I bond, H–C is stronger than H–Si, H–N is stronger than H–P, H–O is stronger than H–S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 8.3.1).
2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C–C single bond is stronger than the Si–Si single bond, which is stronger than the Ge–Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 8.3.1. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N–N, O–O, and F–F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore\[\ce{Cl\bond{-}Cl > Br\bond{-}Br > F\bond{-}F > I–I} \nonumber \] Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

   Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.
4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, e..g, for the SO_4^{2-} ion. In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2.

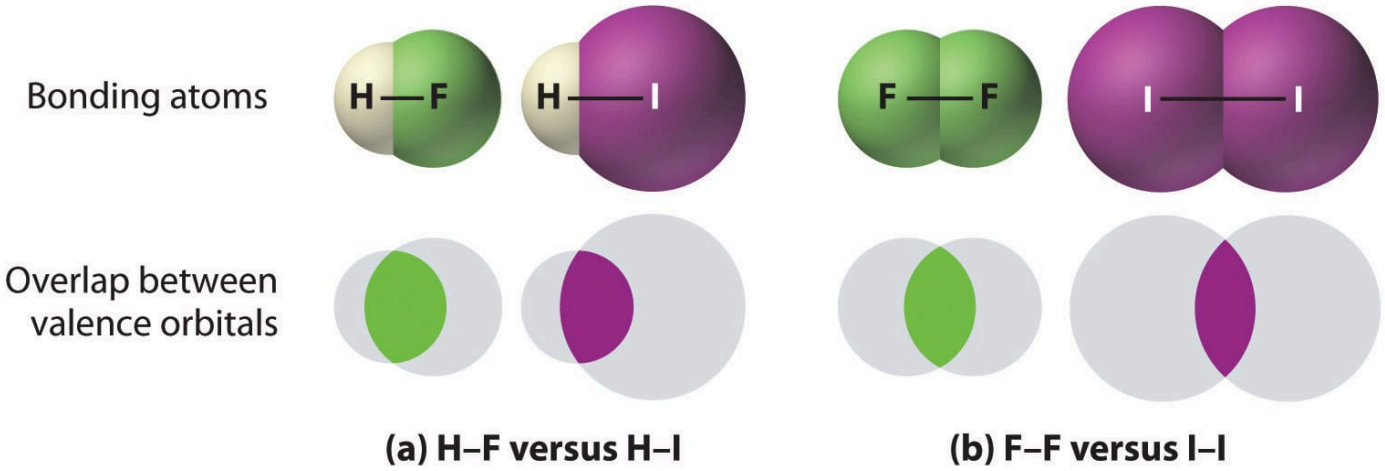


Figure 8.3.1: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space *relative to the size of the bonded atom* decreases; that is, the *percentage* of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

Bond strengths increase as bond order **increases**, while bond distances **decrease**.

The Relationship between Molecular Structure and Bond Energy

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table 8.3.2); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 8.3.2 are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table 8.3.3: Energies for the Dissociation of Successive C–H Bonds in Methane

Reaction	D (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	439
$CH_3(g) \rightarrow CH_2(g) + H(g)$	462
$CH_2(g) \rightarrow CH(g) + H(g)$	424
$CH(g) \rightarrow C(g) + H(g)$	338
Source: Data from *CRC Handbook of Chemistry and Physics* (2004).	

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \tag{8.3.1}$$

The ≈ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn}.

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction

that occurs during the combustion of gasoline:

$$CH_3(CH_2)_5CH_{3(l)} + 11O_{2(g)} \rightarrow 7CO_{2(g)} + 8H_2O_{(g)} \tag{8.3.2}$$

In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

Bonds Broken (kJ/mol) and Bonds Formed (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately –4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481\ \ 7kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f^o values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

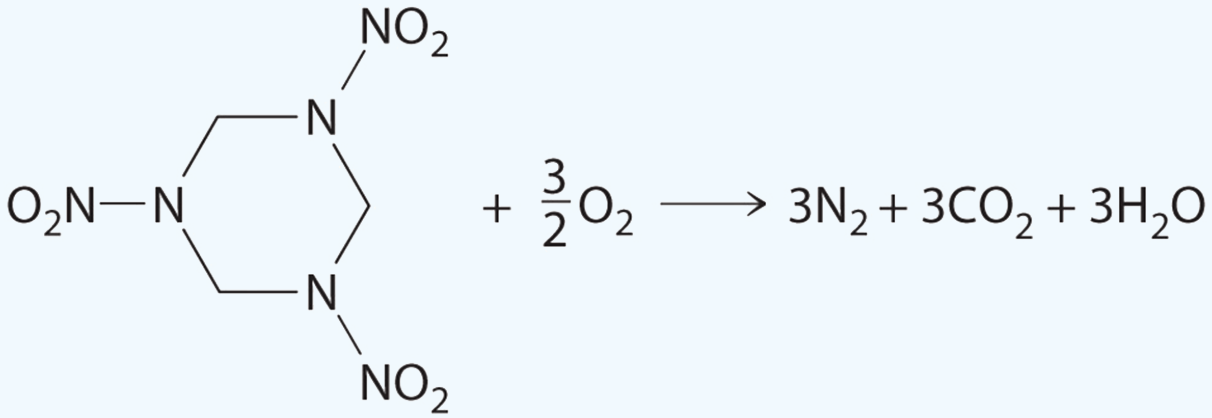
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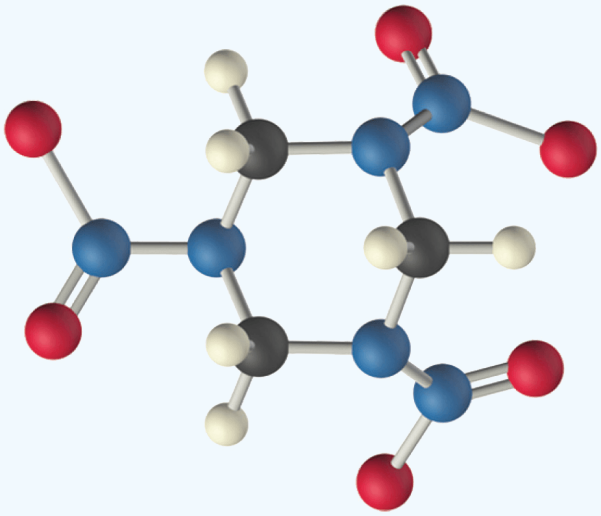
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Example 8.3.1

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 8.3.2 to estimate the ΔH_{rxn} per mole of RDX.



RDX



RDX

Given: chemical reaction, structure of reactant, and Table 8.3.2.

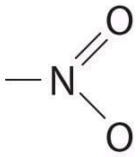
Asked for: ΔH_{rxn} per mole

Strategy:

A. List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.
B. Use Equation 8.3.1 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group ($-NO_2$) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Broken (kJ/mol)	
6 C–H	411 × 6 = 2466	6 C=O	799 × 6 = 4794
3 N–N	167 × 3 = 501	6 O–H	459 × 6 = 2754
3 N–O	201 × 3 = 603		**Total** = 10,374
3 N=O	607 × 3 = 1821		
1.5 O=O	494 × 1.5 = 741		

Bonds Broken (kJ/mol)		Bonds Broken (kJ/mol)	
	Total = 7962		

B From Equation 8.3.1, we have

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed})$$

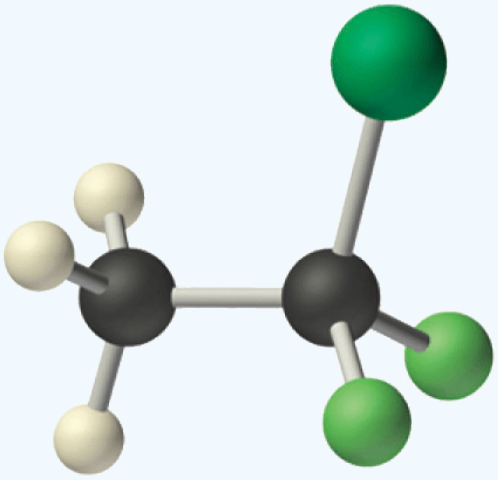
$$= 7962\ kJ/mol - 10,374\ kJ/mol$$

\[=−2412 \;kJ/mol]

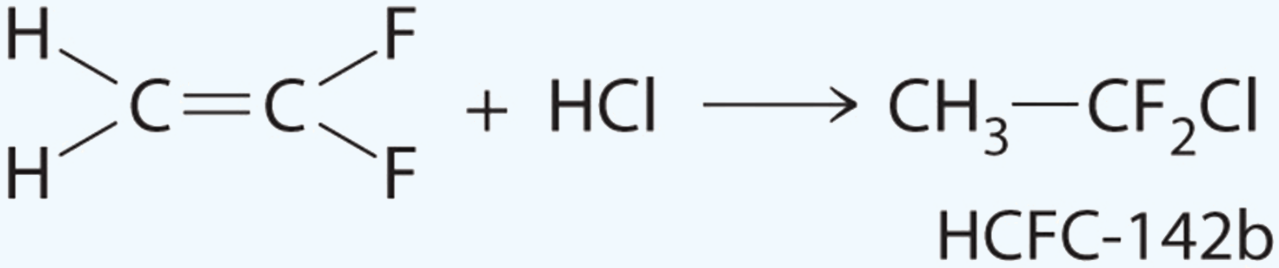
Thus this reaction is also highly exothermic.

Exercise 8.3.1

The molecule HCFC-142b, a hydrochlorofluorocarbon used in place of chlorofluorocarbons (CFCs) such as the Freons, can be prepared by adding HCl to 1,1-difluoroethylene:



HCFC-142b



HCFC-142b

Use tabulated bond energies to calculate ΔH_{rxn}.

Answer available at the end of this section.

Summary

The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms. **Bond order** is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

Contributors and Attributions

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- Wikipedia

Answers

Exercise 8.3.1

–54 kJ/mol

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8.4: Bond Polarity and Electronegativity

Learning Objectives

- To define electronegativity and bond polarity
- To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, while the bonding electron pair is shared equally in the covalent bond in Cl_2, in $NaCl$ the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. As demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity** (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

> Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.

Electronegativity is a function of:

1. the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and
2. the atom's ***electron affinity*** (how strongly the atom attracts other electrons).

Both of these are properties of the *isolated* atom. An element will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always endothermic, or positive for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although

today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

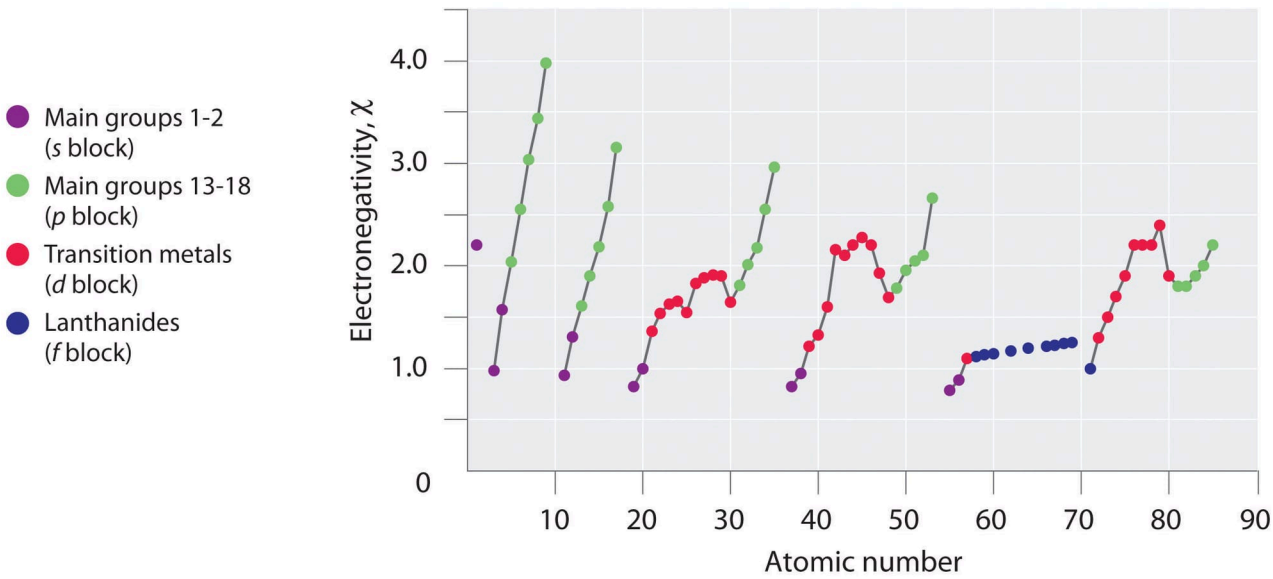
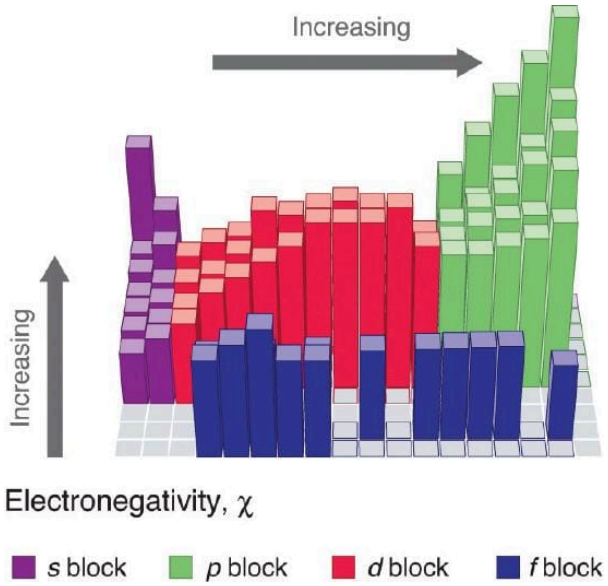


Figure 8.4.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table
The main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

Periodic variations in Pauling's electronegativity values are illustrated in Figures 8.4.1 and 8.4.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).



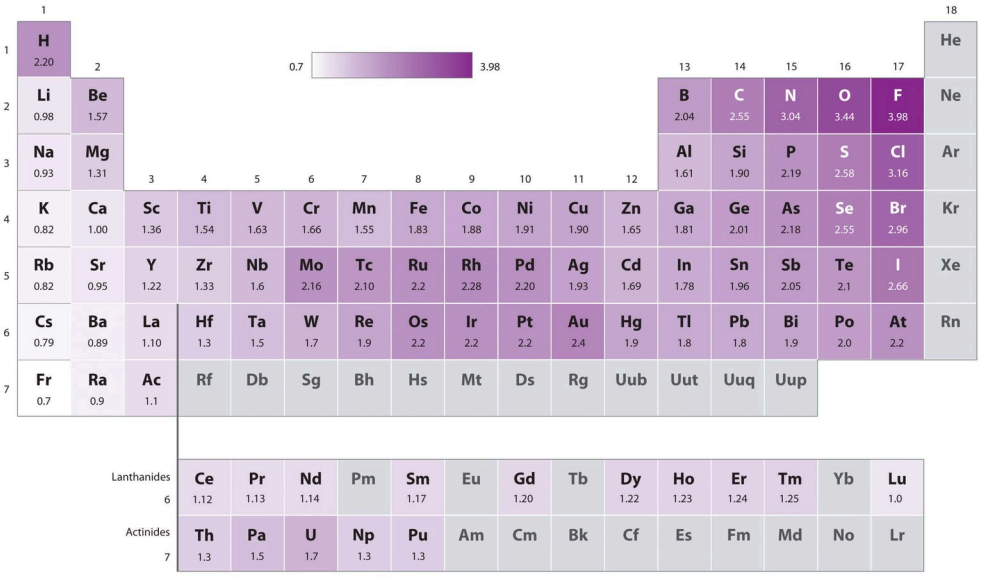
The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electronegativity increase from bottom to top and left to right.

Figure 8.4.2***:*** *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the*

Chemical Bond, 3rd ed. (1960).

Linus Pauling (1901-1994)

When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school, but was later denied a high school degree, and had to work several jobs to put himself through college. Pauling would go on to become one of the most influential chemists of the century if not all time. He won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962.



Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem, e.g., the Mulliken, Allred-Rochow, and Allen electronegativity scales. The Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity, showing the relationship between electronegativity and these other periodic properties.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$ in Figure $8.4.2$) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities ($\chi \sim 2.0$). These are the **metalloids** (or semimetals), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals

and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure 8.4.3 shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

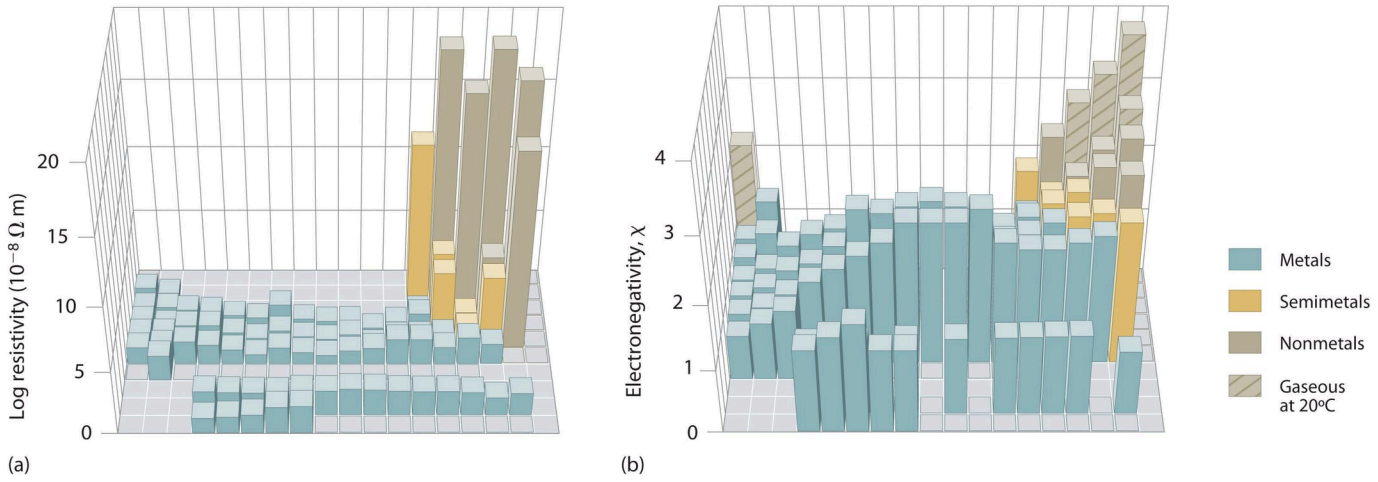


Figure 8.4.3: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

Metals are blue, semimetals are yellow, nonmetals are gray, gaseous at 20 degrees C are gray with dashed lines.

> Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states(opens in new window) are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

Example 8.4.1: Increasing Electronegativity

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.
B. Arrange the elements in order of increasing electronegativity.
C. Classify each element as a metal, a nonmetal, or a metalloid according to its location about the diagonal belt of metalloids running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 8.4.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of metalloids running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a metalloid, and Se and Cl are nonmetals.

Exercise 8.4.1

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Answer available at the end of this section.

Percent Ionic Character of a Covalent polar bond

The two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that electrons are shared unequally between the bonded atoms. Figure 8.4.4 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a polar bond.

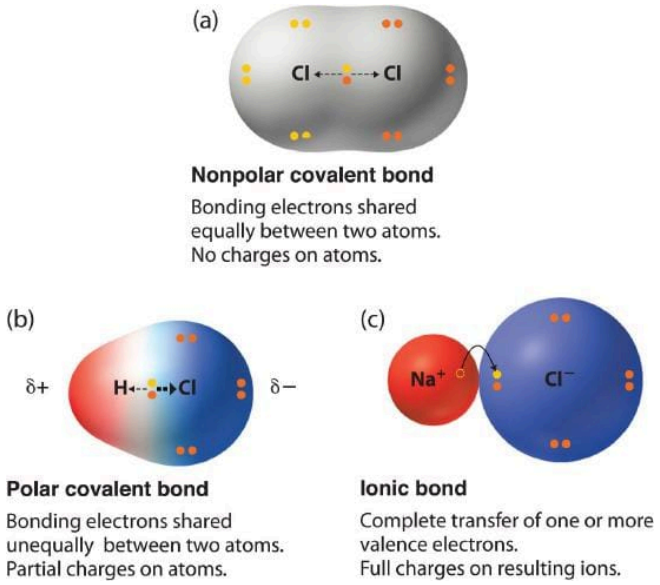


Figure 8.4.4: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{less\ electronegative}{A}} - \underset{\delta^-}{\overset{more\ electronegative}{B}} \tag{8.4.1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

> Bond polarity and ionic character **increase** with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge *Q* on the bonded atoms and the distance *r* between the partial charges:

$$\mu = Qr \tag{8.4.2}$$

where *Q* is measured in coulombs (C) and *r* in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot \cdot m \tag{8.4.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 8.4.4).

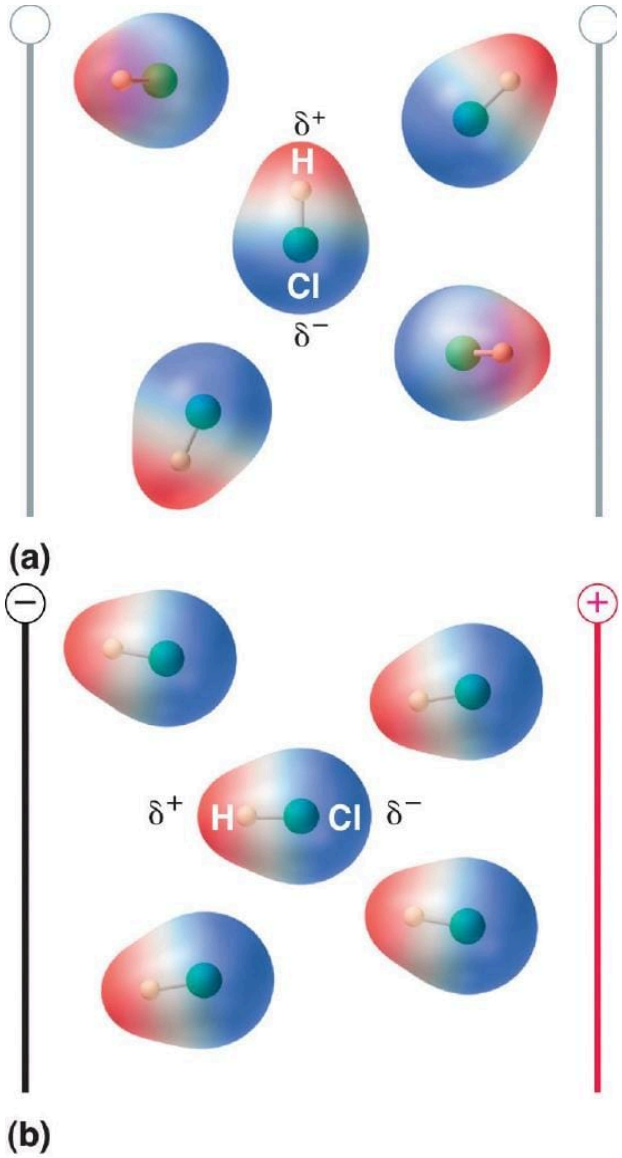


Figure 8.4.5: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field. In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 8.4.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full –1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$Q = \frac{\mu}{r} = 1.109 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{127.8\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 2.901 \times 10^{-20}\ C \tag{8.4.4}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about –0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} = 0.1811\ e^- \tag{8.4.5}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta^+}{H} - \overset{0.18\delta^-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine (χ_H = 2.20; χ_{Cl} = 3.16, $\chi_{Cl} - \chi_H$ = 0.96), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule. Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 8.4.6 shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure 8.4.6 show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 8.4.2.

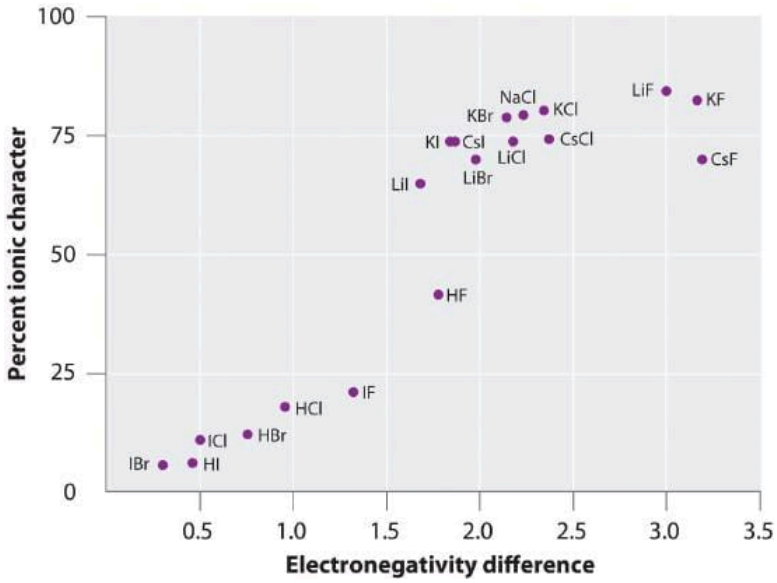


Figure 8.4.6: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 8.4.2

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 8.4.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r} = 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 1.272 \times 10^{-19}\ C$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\% \; ionic \; character = \left(\frac{1.272 \times 10^{-19} \; \cancel{C}}{1.6022 \times 10^{-19} \; \cancel{C}} \right) (100) = 79.39\% \simeq 79\%$$

Exercise 8.4.2

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer available at the end of this section.

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity. The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

Answers

Exercise 8.4.1

Rb < Zr < Ge < N < O; metals (Rb, Zr); metalloid (Ge); nonmetal (N, O)

Exercise 8.4.2

55.5%

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8.5: Drawing Lewis Structures

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure 8.5.1):

- The electrons in the two atoms repel each other because they have the same charge (
- *The electrons in the two atoms repel each other because they have the same charge ($E > 0$).*
- *Similarly, the protons in adjacent atoms repel each other ($E > 0$).*
- *The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa ($E < 0$). Recall that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.*

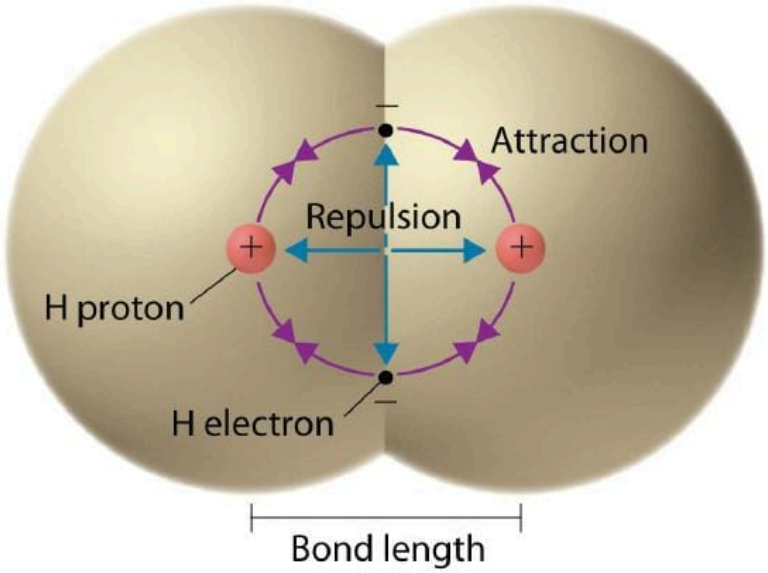


Figure 8.5.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 8.5.2) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figures 8.5.1 and 8.5.2, which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

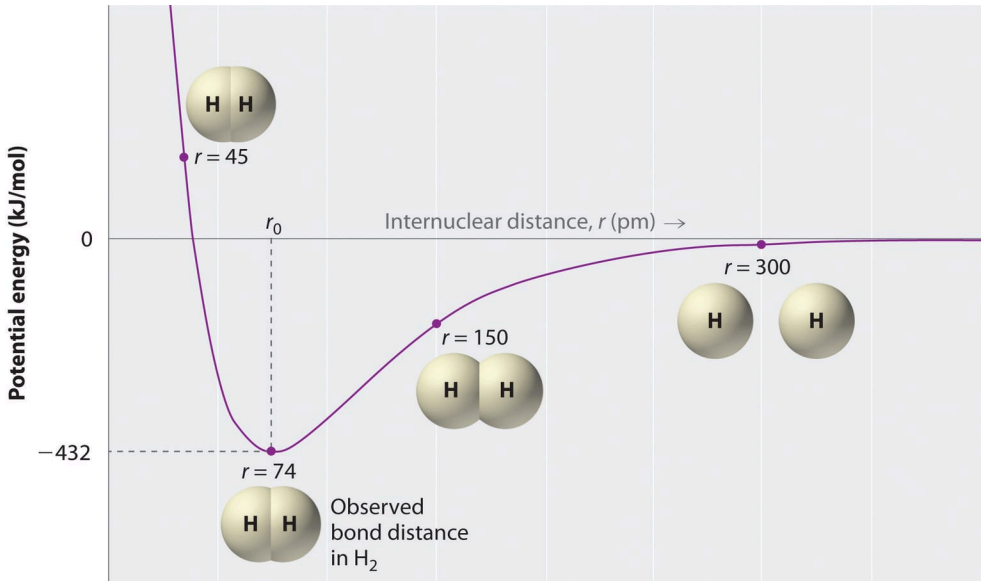


Figure 8.5.2: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

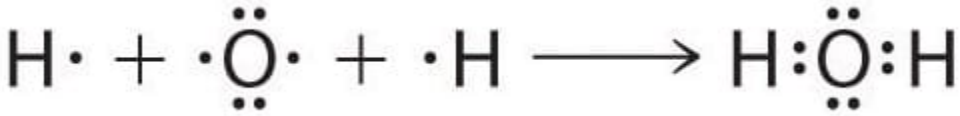
Using Lewis Dot Symbols to Describe Covalent Bonding

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:



Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond. Examples of this type of bonding are presented in Section 8.6 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the –2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^- Ion

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Both the oxygen and chlorine have 3 electron pairs drawn around them with a bond drawn between them. The molecule has square brackets placed around it and has a negative charge.

Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

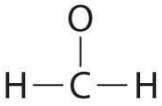
The CH_2O Molecule

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



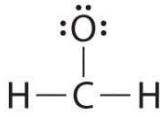
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

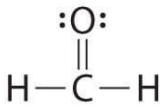
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



The bond between the oxygen and carbon is replaced with a double bond. The oxygen also has two lone pairs drawn.

Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such

a structure is less stable than that shown previously.

Example 8.5.1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

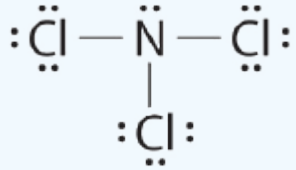
Asked for: Lewis electron structures

Strategy:

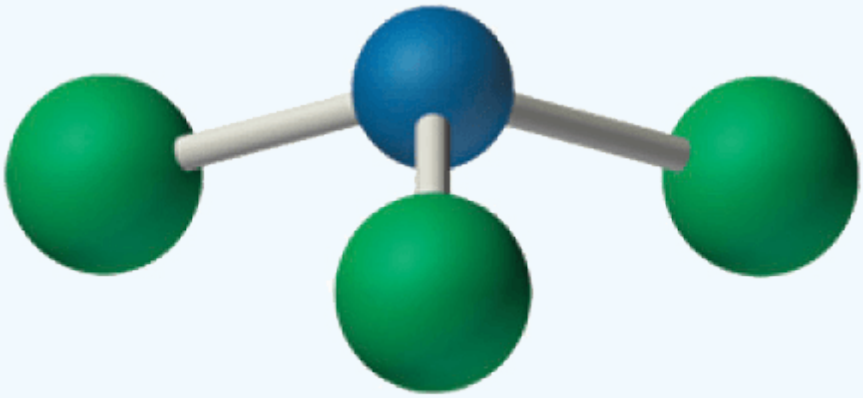
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

a. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

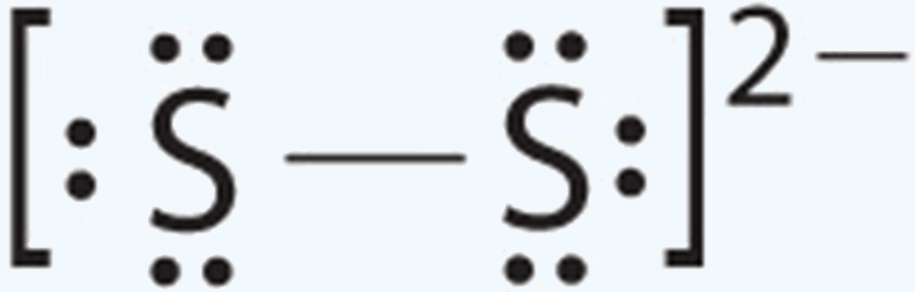


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



Nitrogen trichloride

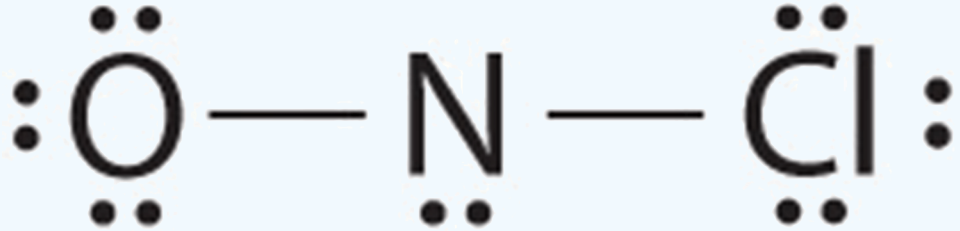
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the –2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



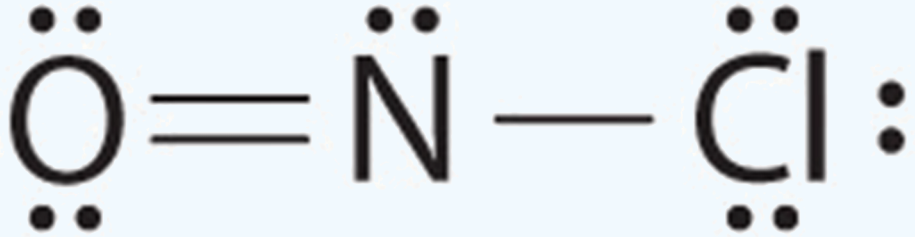
c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



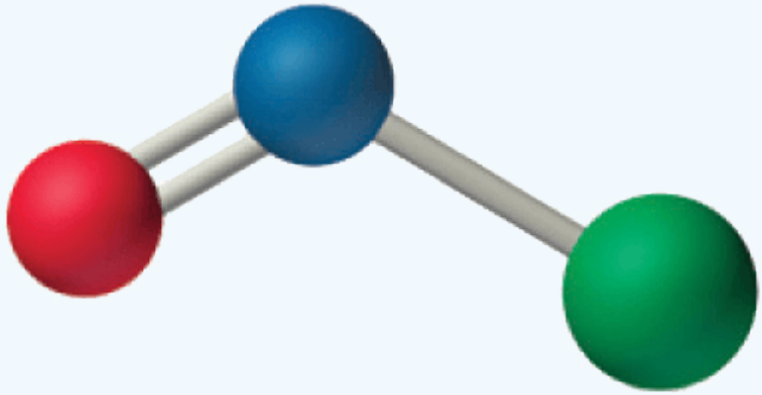
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.

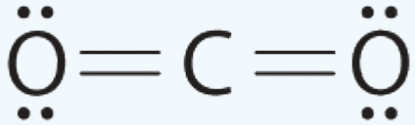


Nitrosyl chloride

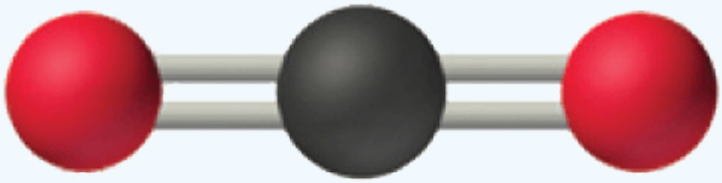
Exercise 8.5.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

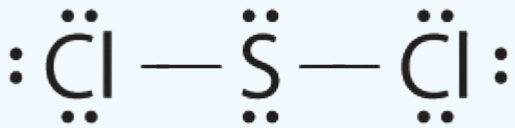
Answer



1.

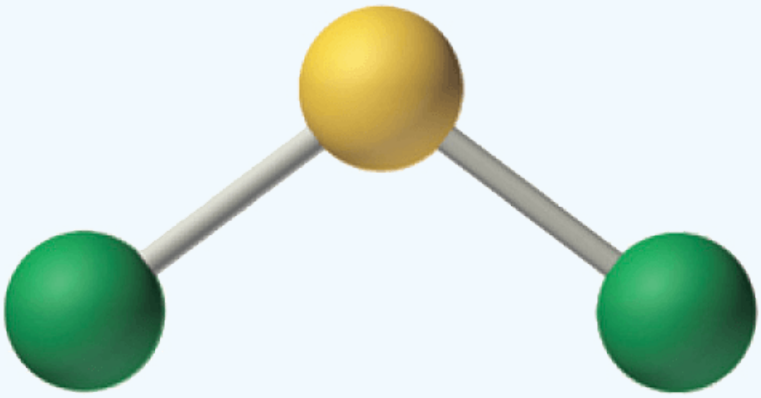


Carbon dioxide



2.

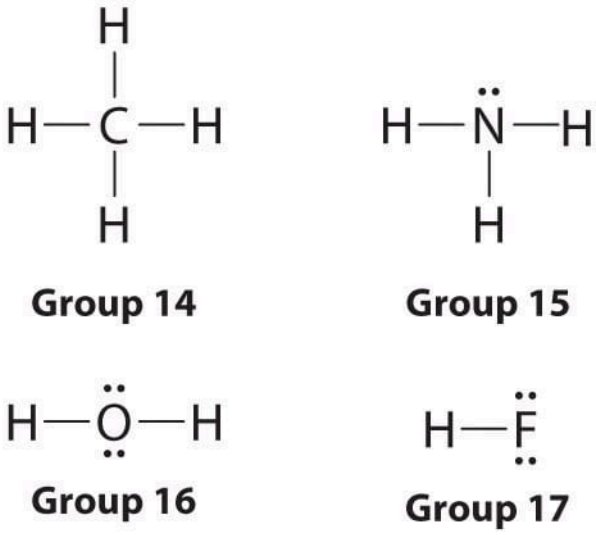
Two chlorines are bonded to a sulfur. The sulfur has 2 lone pairs while the chlorines have 3 lone pairs each.



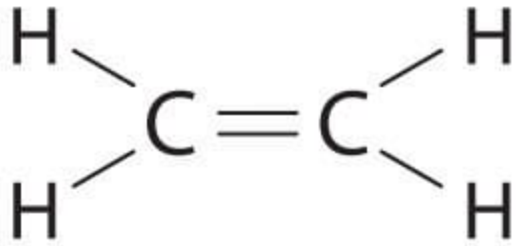
Sulfur dichloride

Using Lewis Electron Structures to Explain Stoichiometry

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of Group 17 (the halogens), this number is one; for the elements of Group 16 (the chalcogens), it is two; for Group 15 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Ethylene

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

> Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 8.5.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

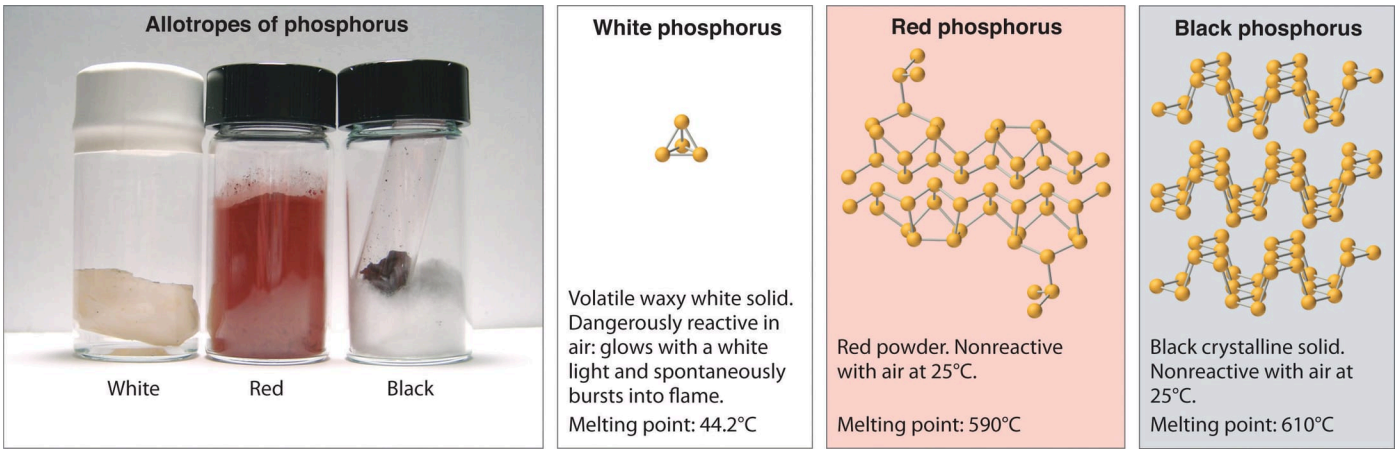


Figure 8.5.3: The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

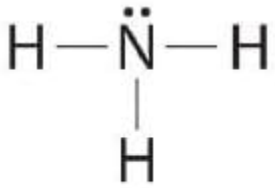
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$formal\ charge = \underset{(free\ atom)}{valence\ e^-} - \underset{(atom\ in\ Lewis\ structure)}{\left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right)} \text{ (atom in Lewis structure)}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding e^-/2)]. Substituting into Equation 8.5.1, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \tag{8.5.1}$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^-/2)]. Using Equation 8.5.1 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \tag{8.5.2}$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

> An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.

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Example 8.5.2: The Ammonium Ion

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

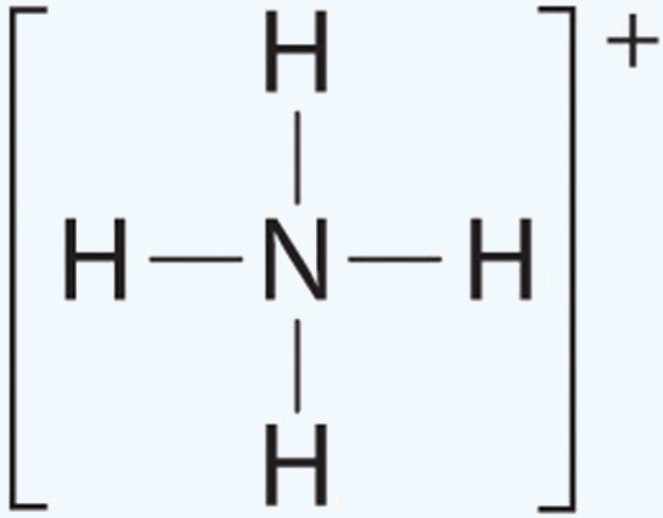
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 8.5.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



The central nitrogen is bonded to four hydrogens. The molecule is surrounded by square brackets. Outside the bracket is where the positive charge is placed.

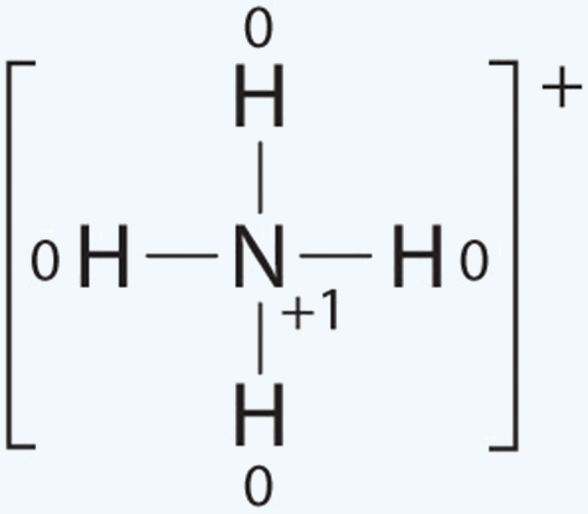
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation ???, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus



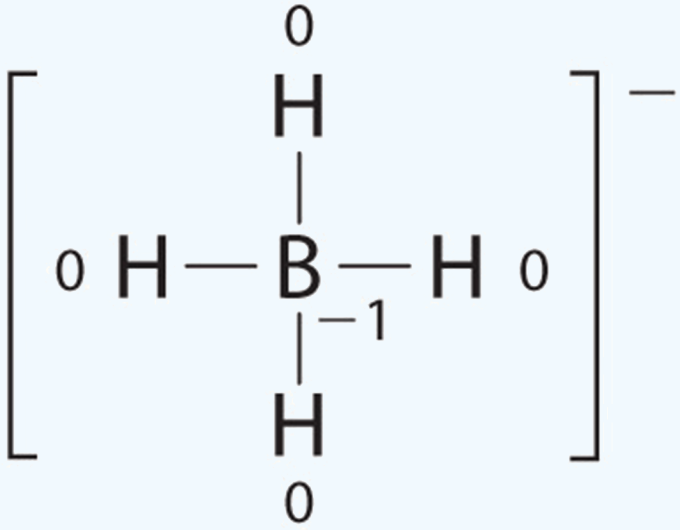
In the Lewis structure, each hydrogen has a zero placed nearby while the nitrogen has a +1 placed nearby.

Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 8.5.2

Write the formal charges on all atoms in BH_4^-.

Answer



Four hydrogens are bonded to a central boron. Each hydrogen has a zero placed nearby while the boron has a -1. The molecule is surrounded by square brackets. Outside of the brackets is a negative charge.

If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable Lewis Structures

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8.6: Resonance Structures

Learning Objectives

- To understand the concept of resonance.

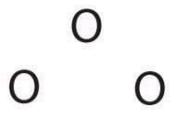
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integral number of covalent bonds.

Sometimes one Lewis Structure is not Enough

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

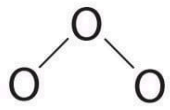
Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



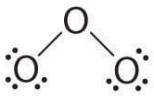
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



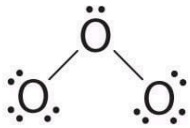
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain



and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

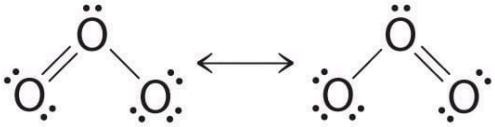


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



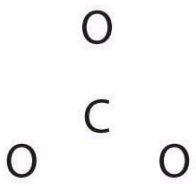
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.

The Carbonate (CO_3^{2-}) Ion

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

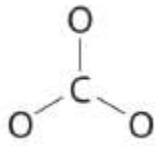
1. Because carbon is the least electronegative element, we place it in the central position:



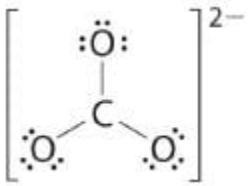
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the –2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:



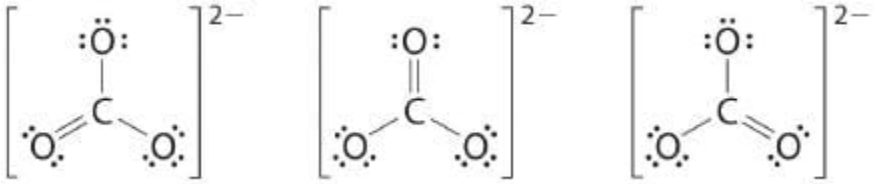
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the –2 charge:



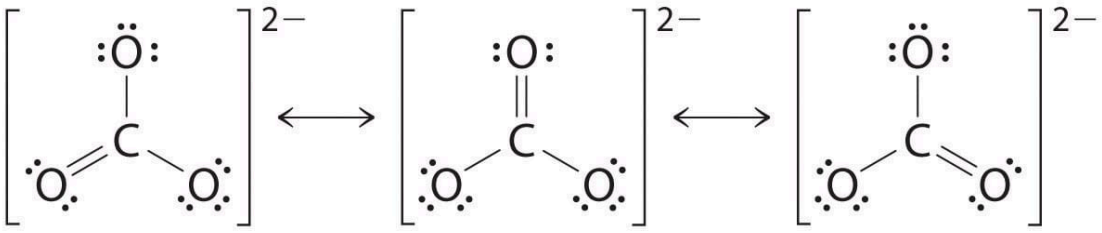
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



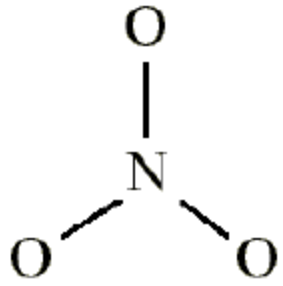
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

The actual structure is an average of these three resonance structures.

The Nitrate (NO_3^-) ion

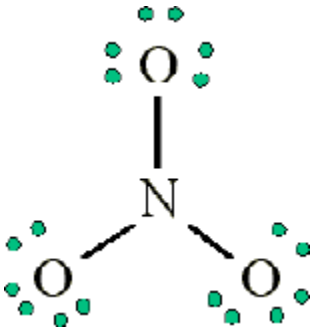
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

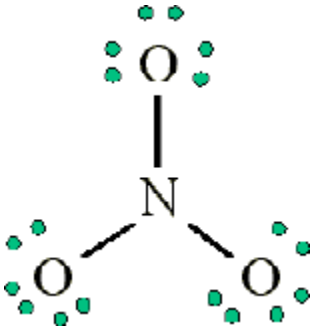


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

3. Add octet electrons to the atoms bonded to the center atom:

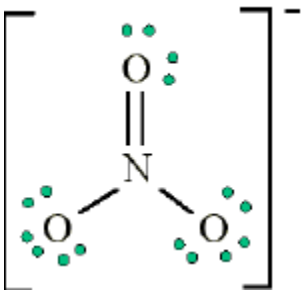


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

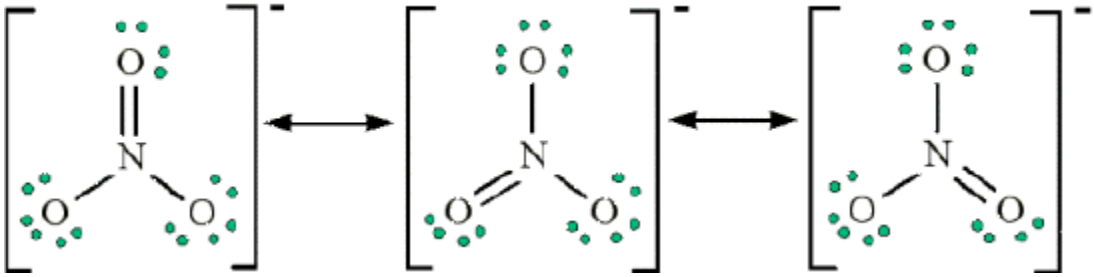
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



A double bond is added between one oxygen and the central nitrogen. The molecule has a negative charge.

6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the NO_3^- ion to be somewhat shorter than a single bond.

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Example 8.6.1: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

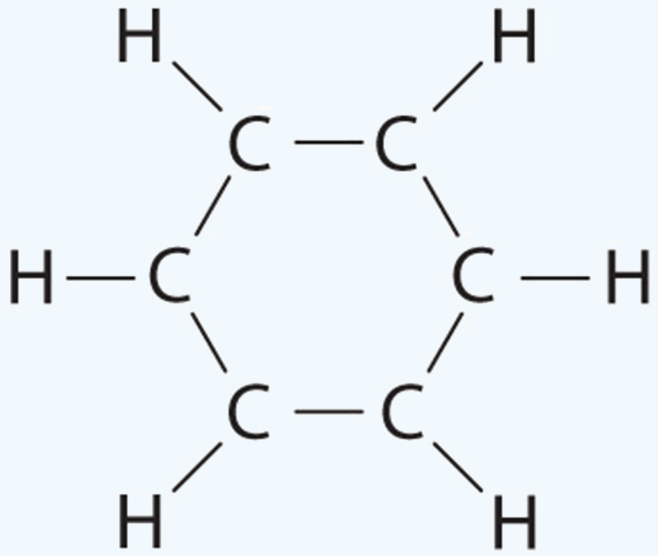
Asked for: resonance structures

Strategy:

A. Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.
B. Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.
C. Draw the resonance structures for benzene.

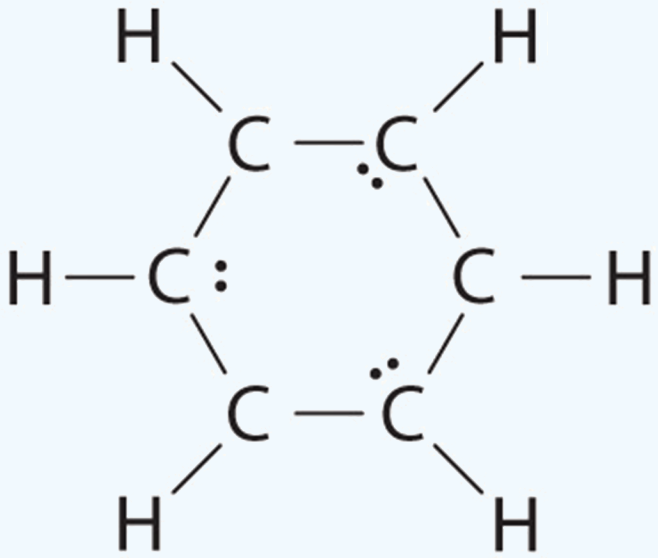
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



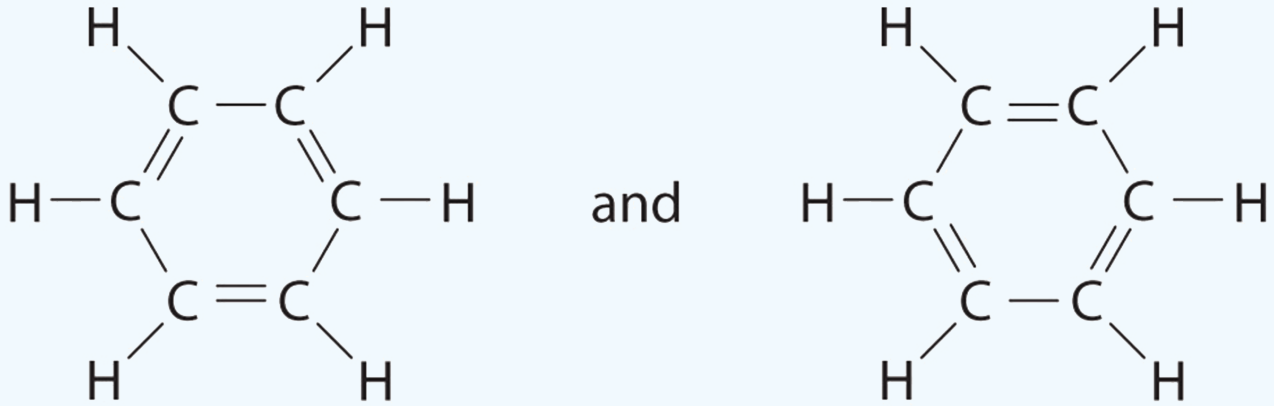
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

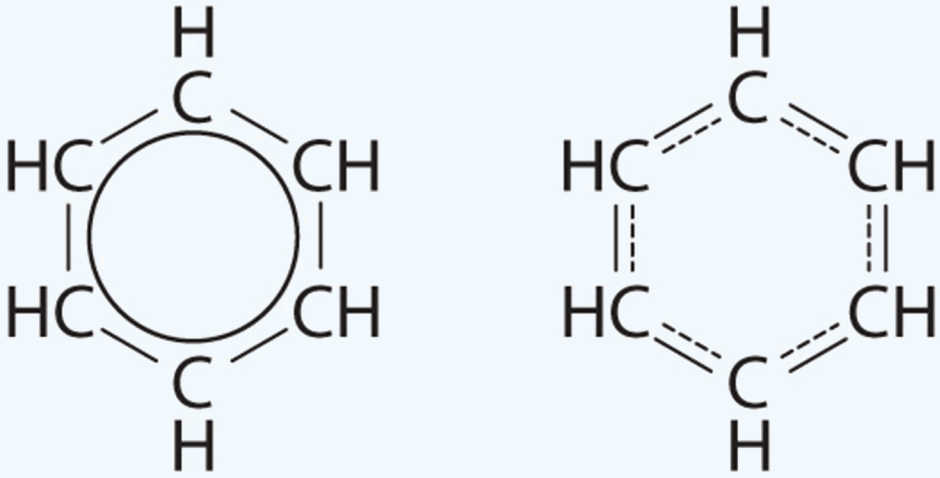


Three carbon atoms now have an octet configuration and a formal charge of –1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



Benzene

Exercise 8.6.1: Nitrite Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer available at the end of this section.

Warning

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example 8.6.1. One would expect the double bonds to be shorter than the single bonds, but if one overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

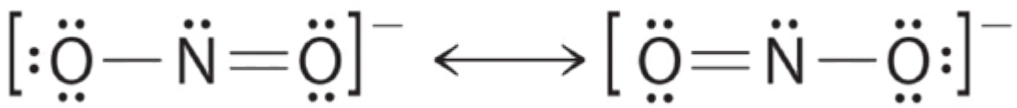
Resonance structures is a mechanism that allows us to use all of the possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms can be in between - a carbon-carbon bond could be mostly single bond with a little bit of double bond character and a partial negative charge, for example.

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

Answers

Exercise 8.6.1**: Nitrite Ion**



There is a double bond between one oxygen and the nitrogen, It can be found on the left oxygen or the right oxygen.

Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

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8.7: Exceptions to the Octet Rule

Learning Objectives

- To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Three cases can be constructed that do not follow the octet rule, and as such, they are known as the exceptions to the octet rule. Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. However, it is hard to imagine that one rule could be followed by all molecules. There is always an exception, and in this case, three exceptions:

1. When there are an odd number of valence electrons
2. When there are too few valence electrons
3. When there are too many valence electrons

Exception 1: Species with Odd Numbers of Electrons

The first exception to the Octet Rule is when there are an odd number of valence electrons. An example of this would be Nitrogen (II) Oxide also called nitric oxide (NO. Nitrogen has 5 valence electrons while Oxygen has 6. The total would be 11 valence electrons to be used. The Octet Rule for this molecule is fulfilled in the above example, however that is with 10 valence electrons. The last one does not know where to go. The lone electron is called an unpaired electron. But where should the unpaired electron go? The unpaired electron is usually placed in the Lewis Dot Structure so that each element in the structure will have the *lowest* formal charge possible. The formal charge is *the perceived charge on an individual atom in a molecule when atoms do not contribute equal numbers of electrons to the bonds they participate in*.

No formal charge at all is the most ideal situation. An example of a stable molecule with an odd number of valence electrons would be nitric oxide. nitric oxide has 11 valence electrons. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitric oxide had ten valence electrons we would come up with the Lewis Structure (Figure $8.7.1$):

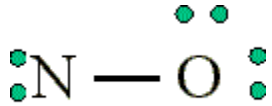


Figure $8.7.1$: This is if nitric oxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure $8.7.2$ based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure $8.7.1$, it has two lone pair electrons and it participates in two bonds (a double bond) with oxygen. This results in nitrogen having a formal charge of +1. Oxygen normally has six valence electrons. In Figure $8.7.1$, oxygen has four lone pair electrons and it participates in two bonds with nitrogen. Oxygen therefore has a formal charge of 0. The overall molecule here has a formal charge of +1 (+1 for nitrogen, 0 for oxygen. +1 + 0 = +1). However, if we add the eleventh electron to nitrogen (because we want the molecule to have the *lowest* total formal charge), it will bring both the nitrogen and the molecule's overall charges to zero, the most ideal formal charge situation. That is exactly what is done to get the correct Lewis structure for nitric oxide (Figure $8.7.2$):

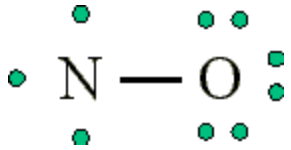


Figure 8.7.2: The proper Lewis structure for NO molecule

Free Radicals

There are actually very few stable molecules with odd numbers of electrons that exist, since that unpaired electron is willing to react with other unpaired electrons. Most odd electron species are highly reactive, which we call Free Radicals. Because of their instability, free radicals bond to atoms in which they can take an electron from in order to become stable, making them very chemically reactive. Radicals are found as both reactants and products, but generally react to form more stable molecules as soon as they can. In order to emphasize the existence of the unpaired electron, radicals are denoted with a dot in front of their chemical symbol as with $\cdot OH$, the hydroxyl radical. An example of a radical you may by familiar with already is the gaseous chlorine atom, denoted $\cdot Cl$. Interestingly, an odd Number of Valence Electrons will result in the molecule being paramagnetic.

Exception 2: Incomplete Octets

The second exception to the Octet Rule is when there are too few valence electrons that results in an incomplete Octet. There are even more occasions where the octet rule does not give the most correct depiction of a molecule or ion. This is also the case with incomplete octets. Species with incomplete octets are pretty rare and generally are only found in some beryllium, aluminum, and boron compounds including the boron hydrides. Let's take a look at one such hydride, BH_3 (Borane).

If one were to make a Lewis structure for BH_3 following the basic strategies for drawing Lewis structures, one would probably come up with this structure (Figure 8.7.2):

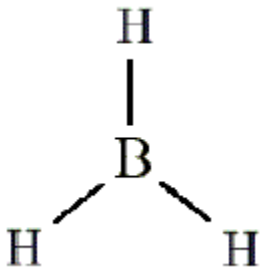


Figure 8.7.3: The structure of BH_3 is square planer.

The problem with this structure is that boron has an incomplete octet; it only has six electrons around it. Hydrogen atoms can naturally only have only 2 electrons in their outermost shell (their version of an octet), and as such there are no spare electrons to form a double bond with boron. One might surmise that the failure of this structure to form complete octets must mean that this bond should be ionic instead of covalent. However, boron has an electronegativity that is very similar to hydrogen, meaning there is likely very little ionic character in the hydrogen to boron bonds, and as such this Lewis structure, though it does not fulfill the octet rule, is likely the best structure possible for depicting BH_3 with Lewis theory. One of the things that may account for BH_3's incomplete octet is that it is commonly a transitory species, formed temporarily in reactions that involve multiple steps.

Let's take a look at another incomplete octet situation dealing with boron, BF_3 (Boron trifluorine). Like with BH_3, the initial drawing of a Lewis structure of BF_3 will form a structure where boron has only six electrons around it (Figure 8.7.4).

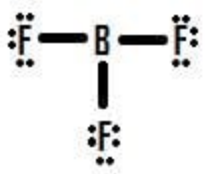


Figure 8.7.4

If you look Figure 8.7.4, you can see that the fluorine atoms possess extra lone pairs that they can use to make additional bonds with boron, and you might think that all you have to do is make one lone pair into a bond and the structure will be correct. If we add one double bond between boron and one of the fluorines we get the following Lewis Structure (Figure 8.7.5):

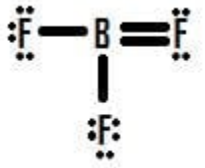


Figure 8.7.5

Each fluorine has eight electrons, and the boron atom has eight as well! Each atom has a perfect octet, right? Not so fast. We must examine the formal charges of this structure. The fluorine that shares a double bond with boron has six electrons around it (four from its two lone pairs of electrons and one each from its two bonds with boron). This is one less electron than the number of valence electrons it would have naturally (Group Seven elements have seven valence electrons), so it has a formal charge of +1. The two flourines that share single bonds with boron have seven electrons around them (six from their three lone pairs and one from their single bonds with boron). This is the same amount as the number of valence electrons they would have on their own, so they both have a formal charge of zero. Finally, boron has four electrons around it (one from each of its four bonds shared with fluorine). This is one more electron than the number of valence electrons that boron would have on its own, and as such boron has a formal charge of -1.

This structure is supported by the fact that the experimentally determined bond length of the boron to fluorine bonds in BF_3 is less than what would be typical for a single bond (see Bond Order and Lengths). However, this structure contradicts one of the major rules of formal charges: Negative formal charges are supposed to be found on the more electronegative atom(s) in a bond, but in the structure depicted in Figure 8.7.5, a *positive* formal charge is found on fluorine, which not only is the most electronegative element in the structure, but the most electronegative element in the entire periodic table ($\chi = 4.0$). Boron on the other hand, with the much lower electronegativity of 2.0, has the negative formal charge in this structure. This formal charge-electronegativity disagreement makes this double-bonded structure impossible.

However the large electronegativity difference here, as opposed to in BH_3, signifies significant polar bonds between boron and fluorine, which means there is a high ionic character to this molecule. This suggests the possibility of a semi-ionic structure such as seen in Figure 8.7.6:

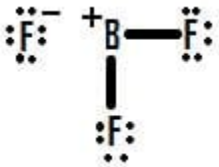


Figure 8.7.6

A bond is broken between one of the fluorine's and the boron making the free fluorine negatively charged and the boron positively charged.

None of these three structures is the "correct" structure in this instance. The most "correct" structure is most likely a resonance of all three structures: the one with the incomplete octet (Figure 8.7.4), the one with the double bond (Figure 8.7.5), and the one with the ionic bond (Figure 8.7.6). The most contributing structure is probably the incomplete octet structure (due to Figure 8.7.5 being basically impossible and Figure 8.7.6 not matching up with the behavior and properties of BF_3). As you can see even when other possibilities exist, incomplete octets may best portray a molecular structure.

As a side note, it is important to note that BF_3 frequently bonds with a F^- ion in order to form BF_4^- rather than staying as BF_3. This structure completes boron's octet and it is more common in nature. This exemplifies the fact that incomplete octets are rare, and other configurations are typically more favorable, including bonding with additional ions as in the case of BF_3 .

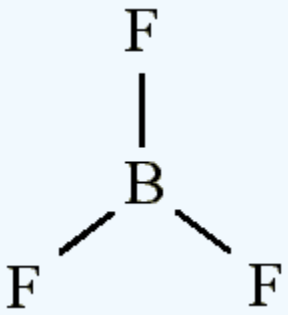
Example 8.7.1**:** NF_3

Draw the Lewis structure for boron trifluoride (BF_3).

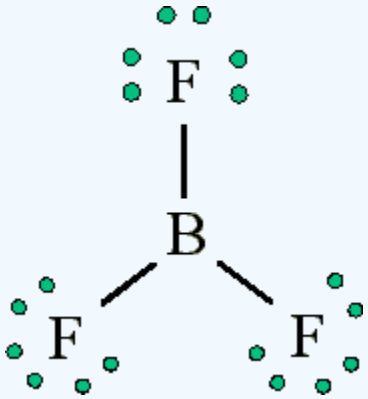
Solution

1. Add electrons (3*7) + 3 = **24**

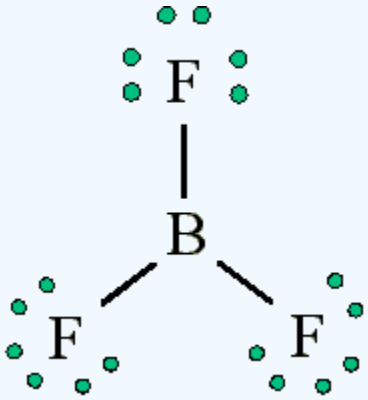
2. Draw connectivities:



3. Add octets to outer atoms:

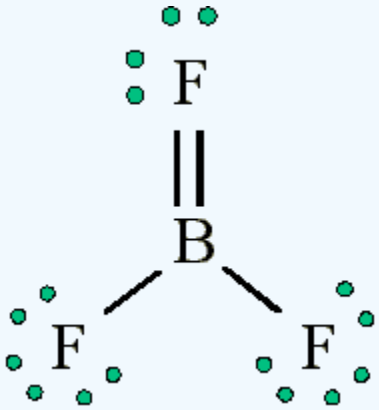


4. Add extra electrons (24-24=0) to central atom:



5. Does central electron have octet?

- NO. It has 6 electrons
- Add a multiple bond (double bond) to see if central atom can achieve an octet:

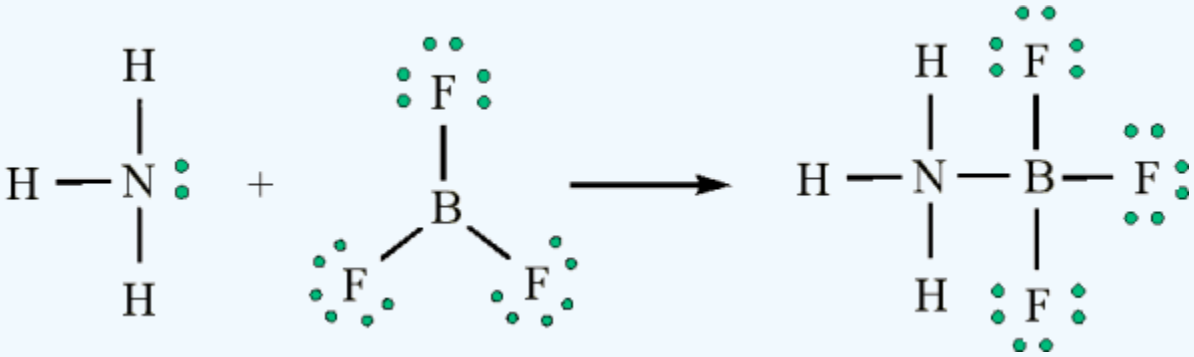


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

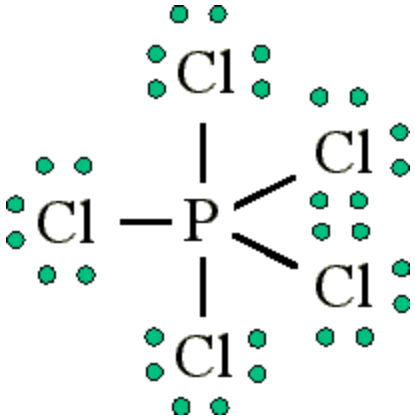
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single bonds, and 6 valence electrons around the central boron is the most likely structure***

BF_3 reacts strongly with compounds which have an unshared pair of electrons which can be used to form a bond with the boron:



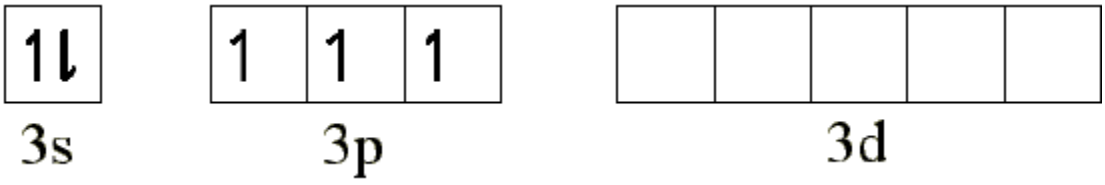
Exception 3: Expanded Valence Shells

More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, and a nonmetal central atom found in the third period or below*, which those terminal atoms bond to. For example, PCl_5 is a legitimate compound (whereas NCl_5) is not:



> Expanded valence shells are observed **only** for elements in period 3 (i.e. n=3) and beyond

The 'octet' rule is based upon available ns and n*p* orbitals for valence electrons (2 electrons in the *s* orbitals, and 6 in the *p* orbitals). Beginning with the n=3 principle quantum number, the d orbitals become available (*l*=2). The orbital diagram for the valence shell of phosphorous is:



Hence, the third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons. Size is also an important consideration:

- The larger the central atom, the larger the number of electrons which can surround it
- Expanded valence shells occur most often when the central atom is bonded to small electronegative atoms, such as F, Cl and O.

There is currently much scientific exploration and inquiry into the reason why expanded valence shells are found. The top area of interest is figuring out where the extra pair(s) of electrons are found. Many chemists think that there is not a very large energy difference between the 3p and 3d orbitals, and as such it is plausible for extra electrons to easily fill the 3d orbital when an expanded octet is more favorable than having a complete octet. This matter is still under hot debate, however and there is even debate as to what makes an expanded octet more favorable than a configuration that follows the octet rule.

One of the situations where expanded octet structures are treated as more favorable than Lewis structures that follow the octet rule is when the formal charges in the expanded octet structure are smaller than in a structure that adheres to the octet rule, or when there are less formal charges in the expanded octet than in the structure a structure that adheres to the octet rule.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Example 8.7.2: The SO_4^{-2} ion

Such is the case for the sulfate ion, SO_4^{-2}. A strict adherence to the octet rule forms the following Lewis structure:

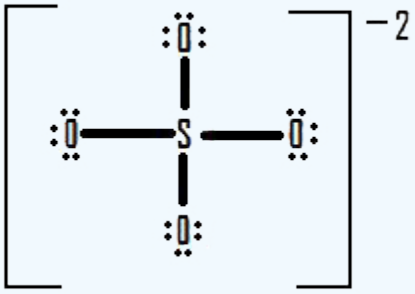


Figure 8.7.12

Four oxygens are bonded to a central sulfur. Each oxygen has 3 lone pairs. The molecule has a minus 2 charge.

If we look at the formal charges on this molecule, we can see that all of the oxygen atoms have seven electrons around them (six from the three lone pairs and one from the bond with sulfur). This is one more electron than the number of valence electrons then they would have normally, and as such each of the oxygens in this structure has a formal charge of -1. Sulfur has four electrons around it in this structure (one from each of its four bonds) which is two electrons more than the number of valence electrons it would have normally, and as such it carries a formal charge of +2.

If instead we made a structure for the sulfate ion with an expanded octet, it would look like this:

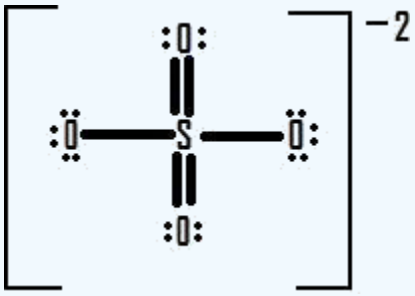


Figure 8.7.13

Looking at the formal charges for this structure, the sulfur ion has six electrons around it (one from each of its bonds). This is the same amount as the number of valence electrons it would have naturally. This leaves sulfur with a formal charge of zero. The two oxygens that have double bonds to sulfur have six electrons each around them (four from the two lone pairs and one each from the two bonds with sulfur). This is the same amount of electrons as the number of valence electrons that oxygen atoms have on their own, and as such both of these oxygen atoms have a formal charge of zero. The two oxygens with the single bonds to sulfur have seven electrons around them in this structure (six from the three lone pairs and one from the bond to sulfur). That is one electron more than the number of valence electrons that oxygen would have on its own, and as such those two oxygens carry a formal charge of -1. Remember that with formal charges, the goal is to keep the formal

charges (or the difference between the formal charges of each atom) as small as possible. The number of and values of the formal charges on this structure (-1 and 0 (difference of 1) in Figure $8.7.12$, as opposed to +2 and -1 (difference of 3) in Figure $8.7.12$) is significantly lower than on the structure that follows the octet rule, and as such an expanded octet is plausible, and even preferred to a normal octet, in this case.

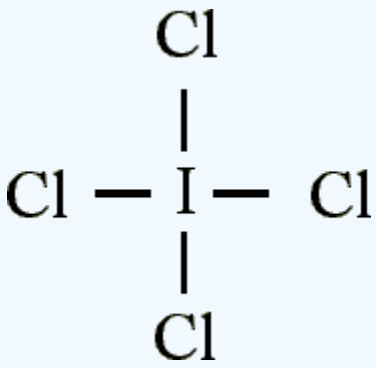
Example $8.7.3$: The ICl_4^- Ion

Draw the Lewis structure for ICl_4^- ion.

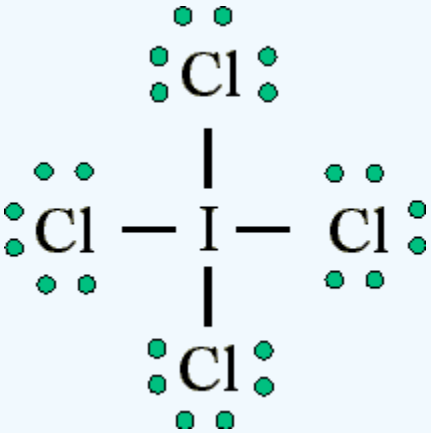
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

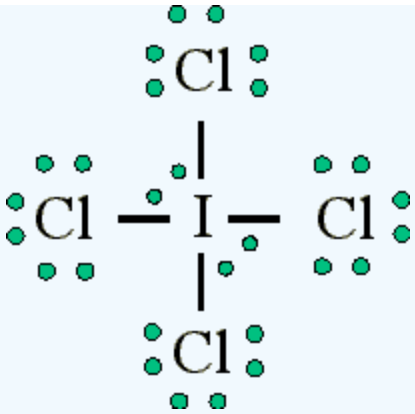
2. Draw the connectivities:



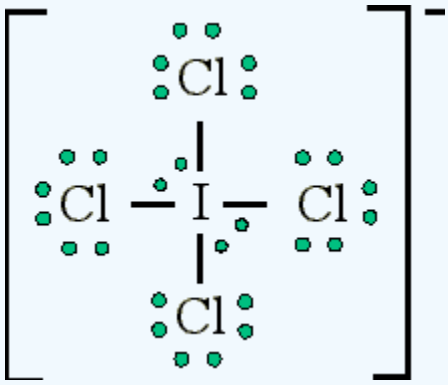
3. Add octet of electrons to outer atoms:



4. Add extra electrons (36-32=**4**) to central atom:



5. The ICl_4^- ion thus has 12 valence electrons around the central Iodine (in the 5*d* orbitals)



Expanded Lewis structures are also plausible depictions of molecules when experimentally determined bond lengths suggest partial double bond characters even when single bonds would already fully fill the octet of the central atom. Despite the cases for expanded octets, as mentioned for incomplete octets, it is important to keep in mind that, in general, the octet rule applies.

Summary

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an odd number of valence electrons, (2) When there are too few valence electrons, and (3) when there are too many valence electrons

References

1. Petrucci, Ralph H.; Harwood, William S.; Herring, F. G.; Madura, Jeffrey D. General Chemistry: Principles & Modern Applications. 9th Ed. New Jersey. Pearson Education, Inc. 2007.
2. Moore, John W.; Stanitski, Conrad L.; Jurs, Peter C. Chemistry; The Molecular Science. 2nd Ed. 2004.

Contributors and Attributions

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8.8: Strength of Covalent Bonds

Learning Objectives

- The define Bond-dissociation energy (bond energy)
- To correlate bond strength with bond length
- To define and used *average bond energies*

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds. The stability of a molecule is a function of the strength of the covalent bonds holding the atoms together.

The Relationship between Bond Order and Bond Energy

Triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however. Table 8.8.1 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table 8.8.1: Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										Multiple Bonds	
H–H	432	C–C	346	N–N	≈167	O–O	≈142	F–F	155	C=C	602
H–C	411	C–Si	318	N–O	201	O–F	190	F–Cl	249	C≡C	835
H–Si	318	C–N	305	N–F	283	O–Cl	218	F–Br	249	C=N	615
H–N	386	C–O	358	N–Cl	313	O–Br	201	F–I	278	C≡N	887
H–P	≈322	C–S	272	N–Br	243	O–I	201	Cl–Cl	240	C=O	749
H–O	459	C–F	485	P–P	201	S–S	226	Cl–Br	216	C≡O	1072
H–S	363	C–Cl	327			S–F	284	Cl–I	208	N=N	418
H–F	565	C–Br	285			S–Cl	255	Br–Br	190	N≡N	942
H–Cl	428	C–I	213			S–Br	218	Br–I	175	N=O	607
H–Br	362	Si–Si	222					I–I	149	O=O	494
H–I	295	Si–O	452							S=O	532

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th ed. (1993).

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H–F bond is stronger than an H–I bond, H–C is stronger than H–Si, H–N is stronger than H–P, H–O is stronger than H–S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 8.11).
2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C–C single bond is stronger than the Si–Si single bond, which is stronger than the Ge–Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 8.11. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N–N, O–O, and F–F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore

$$\mathrm{Cl{-}Cl > Br{-}Br > F{-}F > I{-}I}$$

Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

> Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.

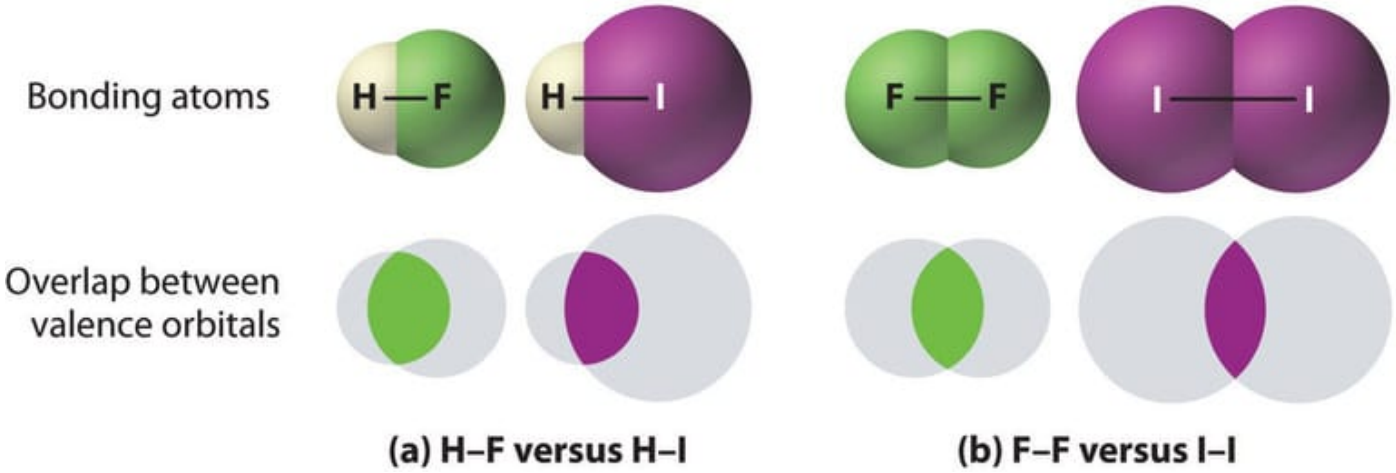


Figure 8.8.1: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space *relative to the size of the bonded atom* decreases; that is, the *percentage* of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, as we discussed for the SO_4^{2-} ion in Section 8.6. In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2.

Bond strengths increase as bond order **increases**, while bond distances **decrease**.

The Relationship between Molecular Structure and Bond Energy

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table 8.8.2); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 8.8.1 are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table 8.8.2: Energies for the Dissociation of Successive C–H Bonds in Methane. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Reaction	D (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	439

Reaction	D (kJ/mol)
$CH_3(g) \rightarrow CH_2(g) + H(g)$	462
$CH_2(g) \rightarrow CH(g) + H(g)$	424
$CH(g) \rightarrow C(g) + H(g)$	338

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \tag{8.8.1}$$

The ≈ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn}.

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction that occurs during the combustion of gasoline:

$$\mathrm{CH_3(CH_2)_5CH_3\,(l) + 11\,O_2\,(g)\ \rightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g)} \tag{8.8.2}$$

In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

Binds Broken (kJ/mol) and Bonds Formed (kJ/mol)

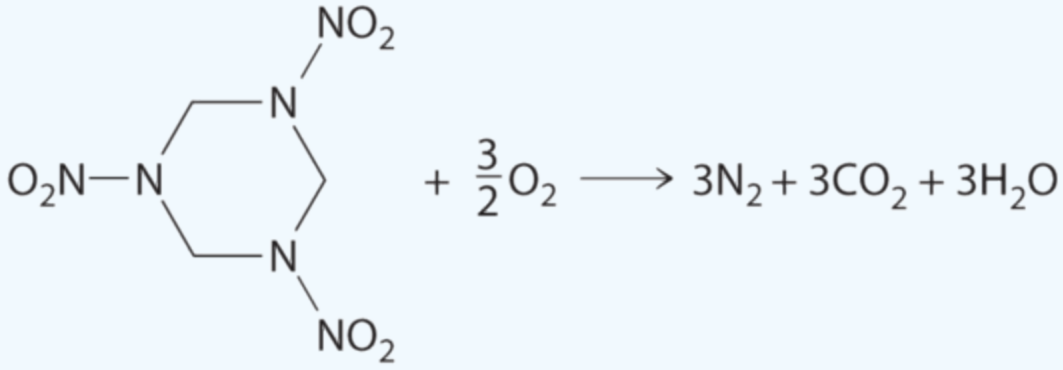
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately –4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481\ \ 7kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f^o values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

Example 8.8.1: Explosives

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 8.8.1 to estimate the ΔH_{rxn} per mole of RDX.



RDX

Given: chemical reaction, structure of reactant, and Table 8.8.1.

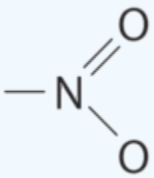
Asked for: ΔH_{rxn} per mole

Strategy:

A. List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.
B. Use Equation 8.8.1 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group (–NO_2) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Broken (kJ/mol)	
6 C–H	411 × 6 = 2466	6 C=O	799 × 6 = 4794
3 N–N	167 × 3 = 501	6 O–H	459 × 6 = 2754
3 N–O	201 × 3 = 603		**Total** = 10,374
3 N=O	607 × 3 = 1821		
1.5 O=O	494 × 1.5 = 741		
	Total = 7962		

B From Equation 8.8.1, we have

$$\begin{aligned}\Delta H_{rxn} &\approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \\ &= 7962\ kJ/mol - 10,374\ kJ/mol \\ &= -2412\ kJ/mol\end{aligned}$$

Thus this reaction is also highly exothermic

Exercise 8.8.1: Freon

The molecule HCFC-142b is a hydrochlorofluorocarbon that is used in place of chlorofluorocarbons (CFCs) such as the Freons and can be prepared by adding HCl to 1,1-difluoroethylene:

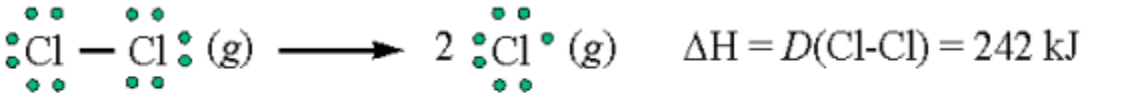
1,1-difluoroethylene reacts with <span class=HCL to produce CH3Cf2Cl and HCFC142b." data-cke-saved-src="/@api/deki/files/129585/imageedit_31_2777381278.png" src="/@api/deki/files/129585/imageedit_31_2777381278.png" data-quail-id="371">

Use tabulated bond energies to calculate ΔH_{rxn}.

Answer available at the end of this section.

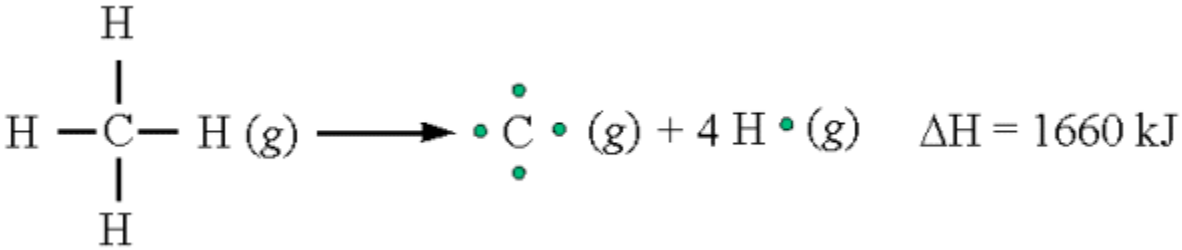
Bond Dissociation Energy

Bond Dissociation Energy (also referred to as Bond energy) is the enthalpy change (ΔH, heat input) required to break a bond (in 1 mole of a gaseous substance)



where "D(Cl-Cl)" represents the bond dissociation energy for the Cl-Cl bond

What about when we have a compound which is not a diatomic molecule? Consider the dissociation of ***methane***:



There are four equivalent C-H bonds, thus we can that the dissociation energy for a single C-H bond would be:

$$\begin{aligned}D(C-H) &= (1660/4)\ kJ/mol \\ &= 415\ kJ/mol\end{aligned}$$

The bond energy for a given bond is influenced by the rest of the molecule. However, this is a relatively small effect (suggesting that bonding electrons are localized between the bonding atoms). Thus, the bond energy for most bonds varies little from the average bonding energy for that type of bond

Bond energy is always a *positive* value - it takes energy to break a covalent bond (conversely energy is released during bond formation)

Table 8.8.4: Average bond energies:

Bond	(kJ/mol)
C-F	485
C-Cl	328
C-Br	276
C-I	240
C-C	348
C-N	293
C-O	358
C-F	485
C-C	348
C=C	614
C≡C	839

The more stable a molecule (i.e. the stronger the bonds) the less likely the molecule is to undergo a chemical reaction.

YouTube Video

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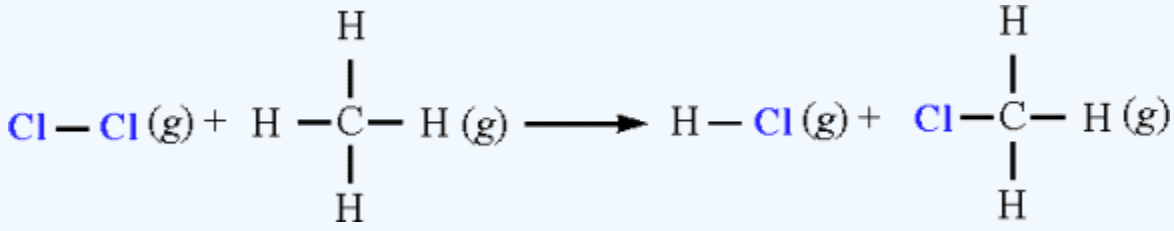
Bond Energies and the Enthalpy of Reactions

If we know which bonds are broken and which bonds are made during a chemical reaction, we can estimate the enthalpy change of the reaction (ΔH_{rxn}) even if we do not know the enthalpies of formation ((ΔH_f^o)for the reactants and products:

$$\Delta H = \sum \text{bond energies of broken bonds} - \sum \text{bond energies of formed bonds} \tag{8.8.3}$$

Example 8.8.2: Chlorination of Methane

What is the enthalpy of reaction between 1 mol of chlorine and 1 mol methane?



Solution

We use Equation 8.8.3, which requires tabulating bonds broken and formed.

- **Bonds broken**: 1 mol of Cl-Cl bonds, 1 mol of C-H bonds
- **Bonds formed**: 1 mol of H-Cl bonds, 1 mol of C-Cl bonds

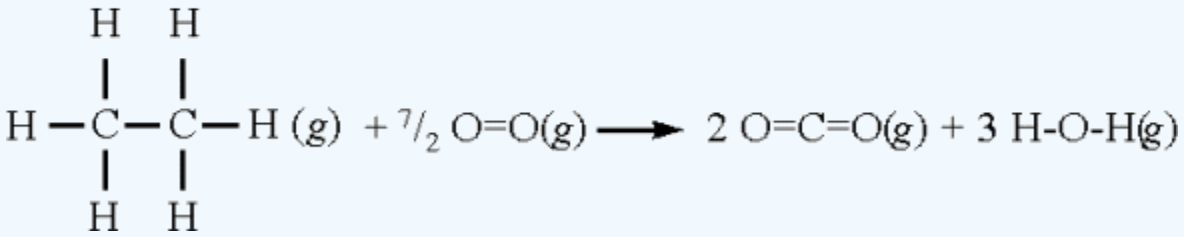
$$\begin{aligned}\Delta H &= [D(Cl-Cl)+D(C-H)]-[D(H-Cl)+D(C-Cl)]\\ &= [242kJ+413kJ]-[431kJ+328kJ]\\ &= -104\,kJ\end{aligned}$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

Example 8.8.3: Combustion of Ethane

What is the enthalpy of reaction for the combustion of 1 mol of ethane?

$$C_2H_6(g) + {}^7/_2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$



Solution

We use Equation 8.8.3, which requires tabulating bonds broken and formed.

- **bonds broken**: 6 moles C-H bonds, 1 mol C-C bonds, $^7/_2$ moles of O=O bonds
- **bonds formed**: 4 moles C=O bonds, 6 moles O-H bonds

$$\begin{aligned}\Delta H &= [(6\times 413)+(348)+(\frac{7}{2}\times 495)]-[(4\times 799)+(6\times 463)]\\ &= 4558-5974\\ &= -1416\,kJ\end{aligned}$$

Therefor the reaction is exothermic.

Table 8.8.5: Bond strength and bond length

Bond	Bond Energy (kJ/mol)	Bond Length (Å)
C-C	348	1.54
C=C	614	1.34
C≡C	839	1.

As the number of bonds between two atoms increases, the bond grows shorter and stronger

Summary

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds

with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

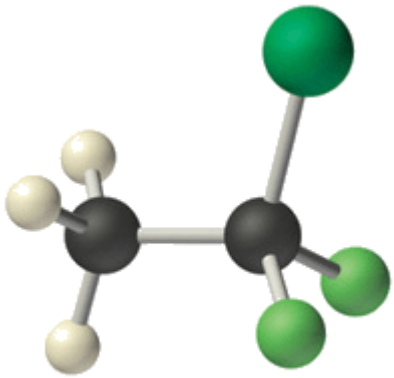
The breakage and formation of bonds is similar to a relationship: you can either get married or divorced and it is more favorable to be married.

- Energy is always **released** to make bonds, which is why the enthalpy change for breaking bonds is always **positive**.
- Energy is always **required** to break bonds. Atoms are much happier when they are "married" and release energy because it is easier and more stable to be in a relationship (e.g., to generate *octet electronic configurations*). The enthalpy change is always **negative** because the system is releasing energy when forming bond.

Answers

Exercise 8.8.1**: Freon**

–54 kJ/mol



HCFC-142b

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8.E: Basic Concepts of Chemical Bonding (Exercises)

8.1: CHEMICAL BONDS, LEWIS SYMBOLS AND THE OCTET RULE

Conceptual Problems

1. The Lewis electron system is a simplified approach for understanding bonding in covalent and ionic compounds. Why do chemists still find it useful?
2. Is a Lewis dot symbol an exact representation of the valence electrons in an atom or ion? Explain your answer.
3. How can the Lewis electron dot system help to predict the stoichiometry of a compound and its chemical and physical properties?
4. How is a Lewis dot symbol consistent with the quantum mechanical model of the atom? How is it different?

Conceptual Answer

3. Lewis dot symbols allow us to predict the number of bonds atoms will form, and therefore the stoichiometry of a compound. The Lewis structure of a compound also indicates the presence or absence of lone pairs of electrons, which provides information on the compound's chemical reactivity and physical properties.

8.2: IONIC BONDING

Conceptual Problems

1. Describe the differences in behavior between NaOH and CH_3OH in aqueous solution. Which solution would be a better conductor of electricity? Explain your reasoning.

2. What is the relationship between the strength of the electrostatic attraction between oppositely charged ions and the distance between the ions? How does the strength of the electrostatic interactions change as the size of the ions increases?

3. Which will result in the release of more energy: the interaction of a gaseous sodium ion with a gaseous oxide ion or the interaction of a gaseous sodium ion with a gaseous bromide ion? Why?

4. Which will result in the release of more energy: the interaction of a gaseous chloride ion with a gaseous sodium ion or a gaseous potassium ion? Explain your answer.

5. What are the predominant interactions when oppositely charged ions are

    1. far apart?
    2. at internuclear distances close to r_0?
    3. very close together (at a distance that is *less* than the sum of the ionic radii)?

6. Several factors contribute to the stability of ionic compounds. Describe one type of interaction that *destabilizes* ionic compounds. Describe the interactions that *stabilize* ionic compounds.

7. What is the relationship between the electrostatic attractive energy between charged particles and the distance between the particles?

Conceptual Answer

1.
2.

3. The interaction of a sodium ion and an oxide ion. The electrostatic attraction energy between ions of opposite charge is

directly proportional to the charge on each ion (Q_1 and Q_2 in Equation 9.1). Thus, more energy is released as the charge on the ions increases (assuming the internuclear distance does not increase substantially). A sodium ion has a +1 charge; an oxide ion, a −2 charge; and a bromide ion, a −1 charge. For the interaction of a sodium ion with an oxide ion, $Q_1 = +1$ and $Q_2 = -2$, whereas for the interaction of a sodium ion with a bromide ion, $Q_1 = +1$ and $Q_2 = -1$. The larger value of $Q_1 \times Q_2$ for the sodium ion–oxide ion interaction means it will release more energy.

Numerical Problems

1. How does the energy of the electrostatic interaction between ions with charges +1 and −1 compare to the interaction between ions with charges +3 and −1 if the distance between the ions is the same in both cases? How does this compare with the magnitude of the interaction between ions with +3 and −3 charges?

2. How many grams of gaseous $MgCl_2$ are needed to give the same electrostatic attractive energy as 0.5 mol of gaseous LiCl? The ionic radii are Li^+ = 76 pm, Mg^{+2} = 72 pm, and Cl^- = 181 pm.

3. Sketch a diagram showing the relationship between potential energy and internuclear distance (from $r = \infty$ to $r = 0$) for the interaction of a bromide ion and a potassium ion to form gaseous KBr. Explain why the energy of the system increases as the distance between the ions decreases from $r = r_0$ to $r = 0$.

4. Calculate the magnitude of the electrostatic attractive energy (E, in kilojoules) for 85.0 g of gaseous SrS ion pairs. The observed internuclear distance in the gas phase is 244.05 pm.

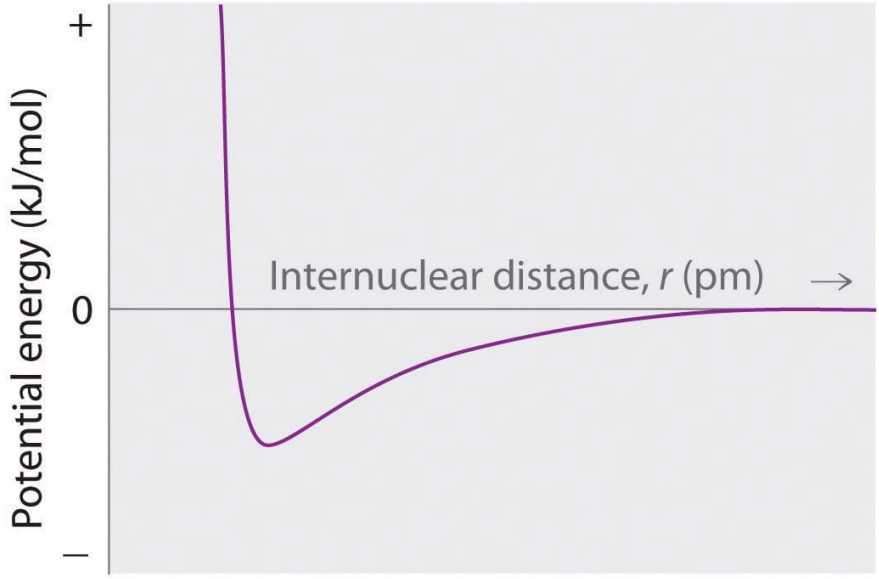
5. What is the electrostatic attractive energy (E, in kilojoules) for 130 g of gaseous HgI_2? The internuclear distance is 255.3 pm.

Numerical Answers

1. According to Equation 9.1, in the first case $Q_1Q_2 = (+1)(-1) = -1$; in the second case, $Q_1Q_2 = (+3)(-1) = -3$. Thus, E will be three times larger for the +3/−1 ions. For +3/−3 ions, $Q_1Q_2 = (+3)(-3) = -9$, so E will be nine times larger than for the +1/−1 ions.

2.

3.



At $r < r_0$, the energy of the system increases due to electron–electron repulsions between the overlapping electron distributions on *adjacent* ions. At very short internuclear distances, electrostatic repulsions between adjacent *nuclei* also become important.

8.3: COVALENT BONDING

Conceptual Problems

1. Which would you expect to be stronger—an S–S bond or an Se–Se bond? Why?
2. Which element—nitrogen, phosphorus, or arsenic—will form the strongest multiple bond with oxygen? Why?
3. Why do multiple bonds between oxygen and period 3 elements tend to be unusually strong?
4. What can bond energies tell you about reactivity?
5. Bond energies are typically reported as average values for a range of bonds in a molecule rather than as specific values for a single bond? Why?
6. If the bonds in the products are weaker than those in the reactants, is a reaction exothermic or endothermic? Explain your answer.
7. A student presumed that because heat was required to initiate a particular reaction, the reaction product would be stable. Instead, the product exploded. What information might have allowed the student to predict this outcome?

Numerical Problems

1. What is the bond order about the central atom(s) of hydrazine (N_2H_4), nitrogen, and diimide (N_2H_2)? Draw Lewis electron structures for each compound and then arrange these compounds in order of increasing N–N bond distance. Which of these compounds would you expect to have the largest N–N bond energy? Explain your answer.

2. What is the carbon–carbon bond order in ethylene (C_2H_4), BrH_2CCH_2Br, and FCCH? Arrange the compounds in order of increasing C–C bond distance. Which would you expect to have the largest C–C bond energy? Why?

3. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.

    1. P–P, Sb–Sb
    2. Cl–Cl, I–I
    3. O–O, Se–Se
    4. S–S, Cl–Cl
    5. Al–Cl, B–Cl

4. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.

    1. Te–Te, S–S
    2. C–H, Ge–H
    3. Si–Si, P–P
    4. Cl–Cl, F–F
    5. Ga–H, Al–H

5. Approximately how much energy per mole is required to completely dissociate acetone [$(CH_3)_2CO$] and urea [$(NH_2)_2CO$] into their constituent atoms?

6. Approximately how much energy per mole is required to completely dissociate ethanol, formaldehyde, and hydrazine into their constituent atoms?

7. Is the reaction of diimine (N_2H_2) with oxygen to produce nitrogen and water exothermic or endothermic? Quantify your answer.

Numerical Answer

1. N_2H_4, bond order 1; N_2H_2, bond order 2; N_2, bond order 3; N–N bond distance: $N_2 < N_2H_2 < N_2H_4$; Largest bond energy: N_2; Highest bond order correlates with strongest and shortest bond.

8.4: BOND POLARITY AND ELECRONEGATIVITY

Conceptual Problems

1. Why do ionic compounds such as KI exhibit substantially less than 100% ionic character in the gas phase?

2. Of the compounds LiI and LiF, which would you expect to behave more like a classical ionic compound? Which would have the greater dipole moment in the gas phase? Explain your answers.

Numerical Problems

1. Predict whether each compound is purely covalent, purely ionic, or polar covalent.

    1. RbCl
    2. S_8
    3. $TiCl_2$
    4. $SbCl_3$
    5. LiI
    6. Br_2

2. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.

    1. NO
    2. HF
    3. MgO
    4. $AlCl_3$
    5. SiO_2
    6. the C=O bond in acetone
    7. O_3

3. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.

    1. NaBr
    2. OF_2
    3. BCl_3
    4. the S–S bond in $CH_3CH_2SSCH_2CH_3$
    5. the C–Cl bond in CH_2Cl_2
    6. the O–H bond in CH_3OH
    7. $PtCl_4^{2-}$

4. Classify each species as having 0%–40% ionic character, 40%–60% ionic character, or 60%–100% ionic character based on the type of bonding you would expect. Justify your reasoning.

    1. CaO
    2. S_8
    3. $AlBr_3$
    4. ICl
    5. Na_2S
    6. SiO_2
    7. LiBr

5. If the bond distance in HCl (dipole moment = 1.109 D) were double the actual value of 127.46 pm, what would be the effect on the charge localized on each atom? What would be the percent negative charge on Cl? At the actual bond distance, how would doubling the charge on each atom affect the dipole moment? Would this represent more ionic or covalent character?

6. Calculate the percent ionic character of HF (dipole moment = 1.826 D) if the H–F bond distance is 92 pm.

7. Calculate the percent ionic character of CO (dipole moment = 0.110 D) if the C–O distance is 113 pm.

8. Calculate the percent ionic character of PbS and PbO in the gas phase, given the following information: for PbS, r = 228.69 pm and μ = 3.59 D; for PbO, r = 192.18 pm and μ = 4.64 D. Would you classify these compounds as having covalent or polar covalent bonds in the solid state?

8.5: DRAWING LEWIS STRUCTURES

Conceptual Problems

1. Compare and contrast covalent and ionic compounds with regard to

    1. volatility.
    2. melting point.
    3. electrical conductivity.
    4. physical appearance.

2. What are the similarities between plots of the overall energy versus internuclear distance for an ionic compound and a covalent compound? Why are the plots so similar?

3. Which atom do you expect to be the central atom in each of the following species?

    1. SO_4^{2-}
    2. NH_4^+
    3. BCl_3
    4. SO_2Cl_2

4. Which atom is the central atom in each of the following species?

    1. PCl_3
    2. $CHCl_3$
    3. SO_2
    4. IF_3

5. What is the relationship between the number of bonds typically formed by the period 2 elements in groups 14, 15, and 16 and their Lewis electron structures?

6. Although formal charges do not represent actual charges on atoms in molecules or ions, they are still useful. Why?

Numerical Problems

1. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?

    1. Se
    2. Kr
    3. Li
    4. Sr
    5. H

2. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?

    1. Na
    2. Br
    3. Ne

4. C
5. Ga

3. Based on Lewis dot symbols, predict the preferred oxidation state of Be, F, B, and Cs.
4. Based on Lewis dot symbols, predict the preferred oxidation state of Br, Rb, O, Si, and Sr.
5. Based on Lewis dot symbols, predict how many bonds gallium, silicon, and selenium will form in their neutral compounds.
6. Determine the total number of valence electrons in the following.
    1. Cr
    2. Cu^{+}
    3. NO^{+}
    4. XeF_2
    5. Br_2
    6. CH_2Cl_2
    7. NO_3^{-}
    8. H_3O^{+}
7. Determine the total number of valence electrons in the following.
    1. Ag
    2. Pt^{2+}
    3. H_2S
    4. OH^{-}
    5. I_2
    6. CH_4
    7. SO_4^{2-}
    8. NH_4^{+}.
8. Draw Lewis electron structures for the following.
    1. F_2
    2. SO_2
    3. $AlCl_4^{-}$
    4. SO_3^{2-}
    5. BrCl
    6. XeF_4
    7. NO^{+}
    8. PCl_3
9. Draw Lewis electron structures for the following.
    1. Br_2
    2. CH_3Br
    3. SO_4^{2-}
    4. O_2
    5. S_2^{2-}
    6. BF_3
10. Draw Lewis electron structures for CO_2, NO_2^{-}, SO_2, and NO_2^{+}. From your diagram, predict which pair(s) of compounds have similar electronic structures.

11. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.

    1. K, S
    2. Sr, Br
    3. Al, O
    4. Mg, Cl

12. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.

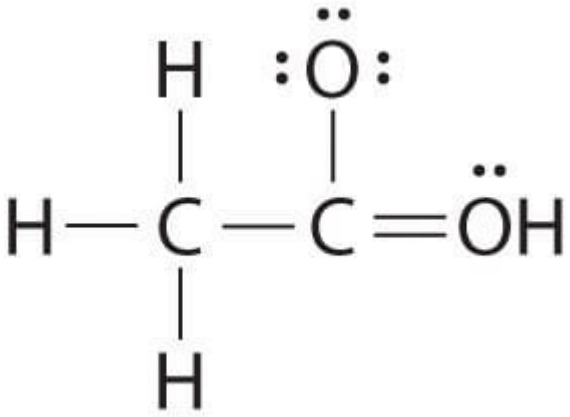
    1. Li, F
    2. Cs, Br
    3. Ca, Cl
    4. B, F

13. Use Lewis dot symbols to predict whether ICl and NO_4^- are chemically reasonable formulas.

14. Draw a plausible Lewis electron structure for a compound with the molecular formula Cl_3PO.

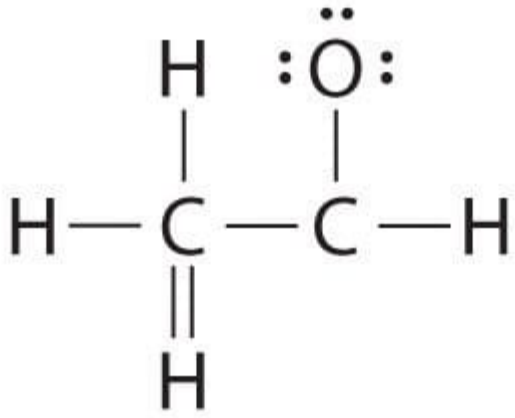
15. Draw a plausible Lewis electron structure for a compound with the molecular formula CH_4O.

16. While reviewing her notes, a student noticed that she had drawn the following structure in her notebook for acetic acid:



    Why is this structure not feasible? Draw an acceptable Lewis structure for acetic acid. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

17. A student proposed the following Lewis structure shown for acetaldehyde.



Why is this structure not feasible? Draw an acceptable Lewis structure for acetaldehyde. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

18. Draw the most likely structure for HCN based on formal charges, showing the formal charge on each atom in your structure. Does this compound have any plausible resonance structures? If so, draw one.

19. Draw the most plausible Lewis structure for NO_3^-. Does this ion have any other resonance structures? Draw at least one other Lewis structure for the nitrate ion that is not plausible based on formal charges.

20. At least two Lewis structures can be drawn for BCl_3. Using arguments based on formal charges, explain why the most likely structure is the one with three B–Cl single bonds.

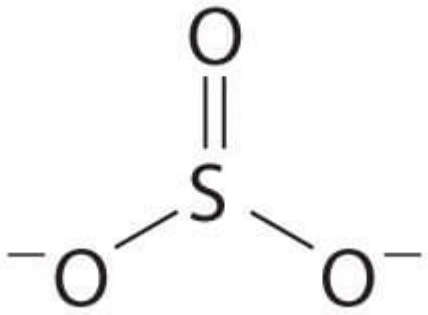
21. Using arguments based on formal charges, explain why the most feasible Lewis structure for SO_4^{2-} has two sulfur–oxygen double bonds.

22. At least two distinct Lewis structures can be drawn for N_3^-. Use arguments based on formal charges to explain why the most likely structure contains a nitrogen–nitrogen double bond.

23. Is H–O–N=O a reasonable structure for the compound HNO_2? Justify your answer using Lewis electron dot structures.

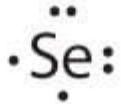
24. Is H–O=C–H a reasonable structure for a compound with the formula CH_2O? Use Lewis electron dot structures to justify your answer.

25. Explain why the following Lewis structure for SO_3^{2-} is or is not reasonable.



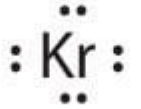
Numerical Answers

1. 1. $[Ar]4s^2 3d^{10} 4p^4$



Selenium can accommodate two more electrons, giving the Se^{2-} ion.

2. $[Ar]4s^2 3d^{10} 4p^6$



Krypton has a closed shell electron configuration, so it cannot accommodate any additional electrons.

3. $1s^2 2s^1$



Lithium can accommodate one additional electron in its 2s orbital, giving the Li^- ion.

4. $[Kr]5s^2$



Strontium has a filled 5s subshell, and additional electrons would have to be placed in an orbital with a higher energy. Thus strontium has no tendency to accept an additional electron.

5. $1s^1$



Hydrogen can accommodate one additional electron in its 1s orbital, giving the H^- ion.

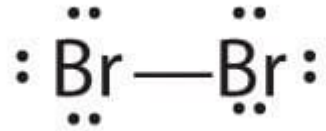
2.

3. Be^{2+}, F^-, B^{3+}, Cs^+

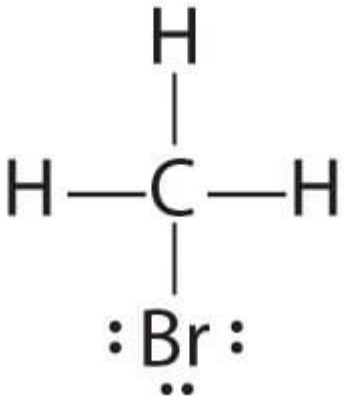
4.
5.
6.
7. 1. 11
   2. 8
   3. 8
   4. 8

5. 14
6. 8
7. 32
8. 8

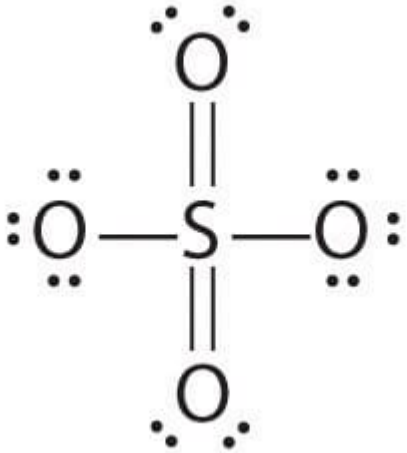
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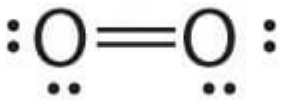
9. 1.



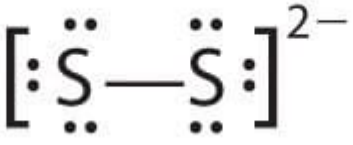
2.



3.

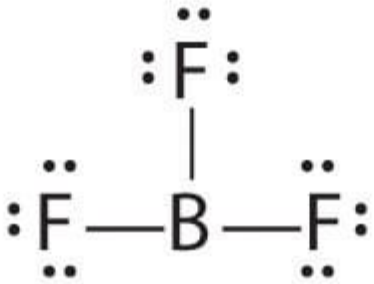


4.



5.

6.



10.



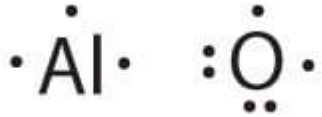
11. 1.

K is the reductant; S is the oxidant. The final stoichiometry is K_2S.



2.

Sr is the reductant; Br is the oxidant. The final stoichiometry is $SrBr_2$.



3.

Al is the reductant; O is the oxidant. The final stoichiometry is Al_2O_3.



4.

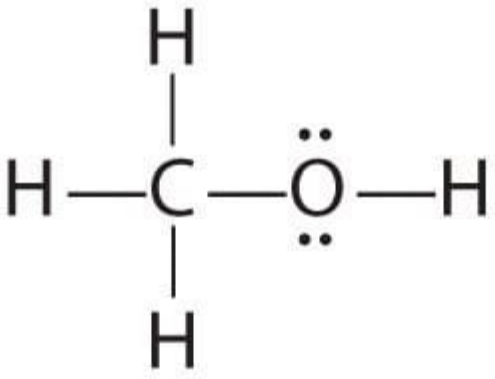
Mg is the reductant; Cl is the oxidant. The final stoichiometry is $MgCl_2$.

12.

13.

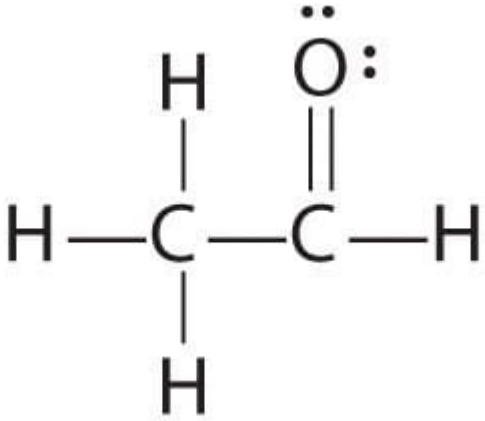
14.

15. The only structure that gives both oxygen and carbon an octet of electrons is the following:

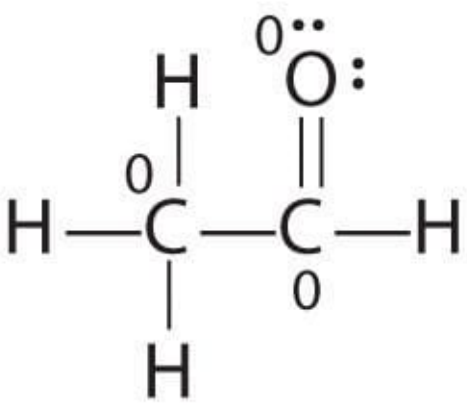


16.

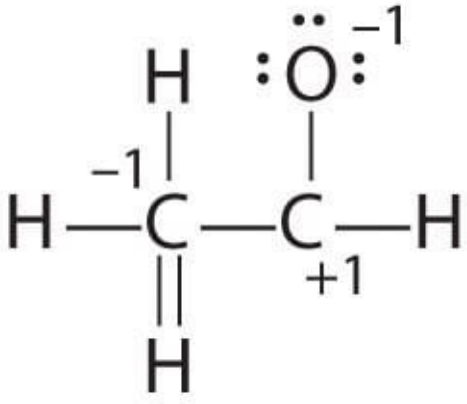
17. The student's proposed structure has two flaws: the hydrogen atom with the double bond has four valence electrons (H can only accommodate two electrons), and the carbon bound to oxygen only has six valence electrons (it should have an octet). An acceptable Lewis structure is



The formal charges on the correct and incorrect structures are as follows:



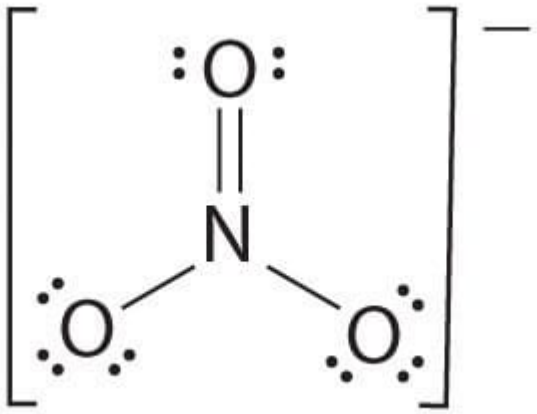
Correct



Incorrect

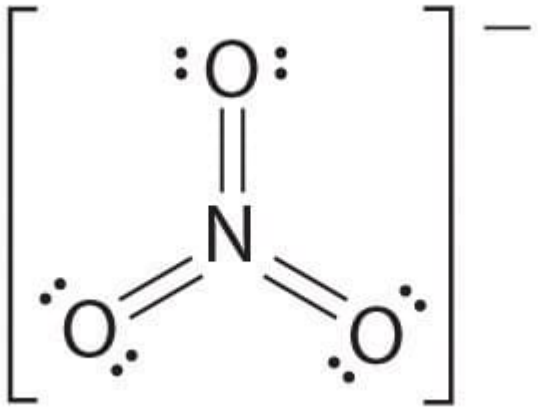
18.

19. The most plausible Lewis structure for NO_3^- is:



There are three equivalent resonance structures for nitrate (only one is shown), in which nitrogen is doubly bonded to one of the three oxygens. In each resonance structure, the formal charge of N is +1; for each singly bonded O, it is –1; and for the doubly bonded oxygen, it is 0.

The following is an example of a Lewis structure that is *not* plausible:



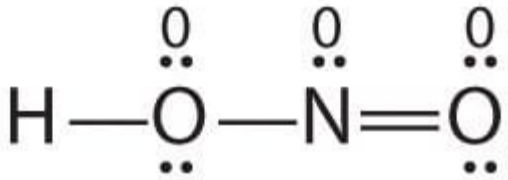
This structure nitrogen has six bonds (nitrogen can form only four bonds) and a formal charge of –1.

20.

21. With four S–O single bonds, each oxygen in SO_4^{2-} has a formal charge of –1, and the central sulfur has a formal charge of +2. With two S=O double bonds, only two oxygens have a formal charge of –1, and sulfur has a formal charge of zero. Lewis structures that minimize formal charges tend to be lowest in energy, making the Lewis structure with two S=O double bonds the most probable.

22.

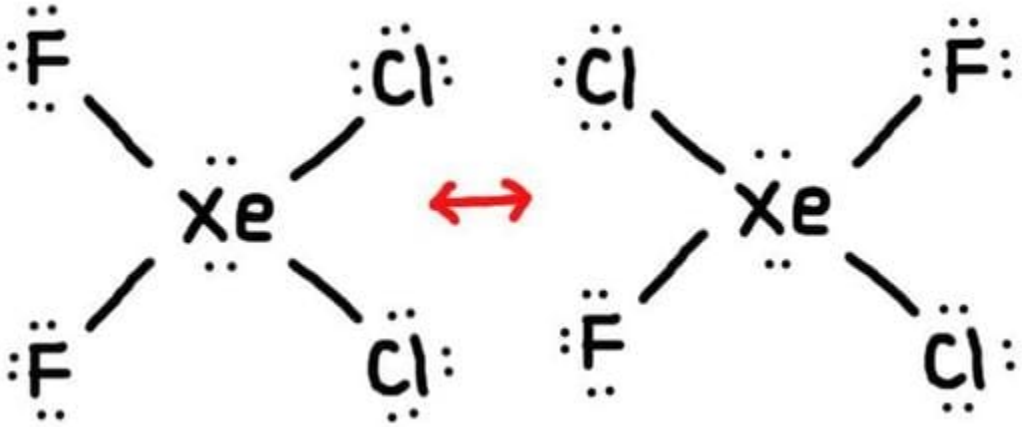
23. Yes. This is a reasonable Lewis structure, because the formal charge on all atoms is zero, and each atom (except H) has an octet of electrons.



8.6: RESONANCE STRUCTURES

Conceptual Problems

1. Why are resonance structures important?
2. In what types of compounds are resonance structures particularly common?
3. True or False, The picture below is a resonance structure?



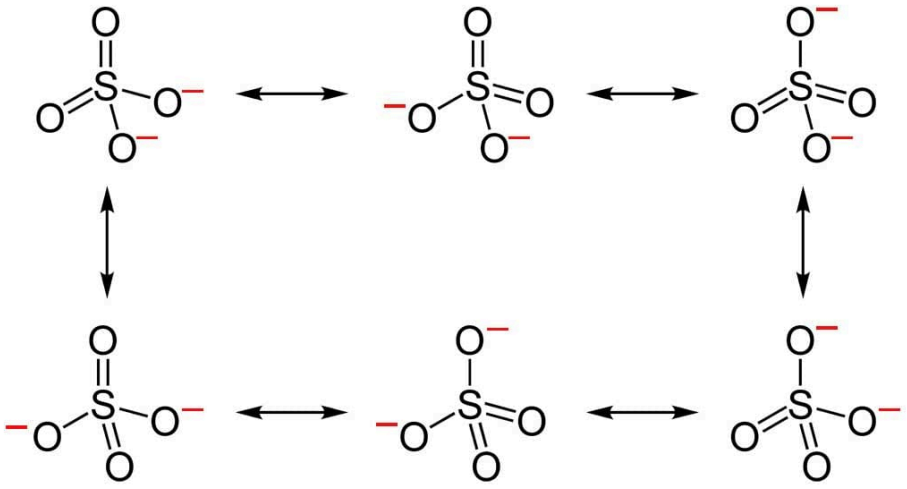
Numerical Problems

1. Draw all the resonance structures for each ion.
   a. HSO_4^-
   b. HSO_3^-
2. Draw the Lewis Dot Structure for **SO_4^{2-}** and all possible resonance structures. Which of the following resonance structure is not favored among the Lewis Structures? Explain why. Assign Formal Charges.
3. Draw the Lewis Dot Structure for **CH_3COO^-** and all possible resonance structures. Assign Formal Charges. Choose the most favorable Lewis Structure.
4. Draw the Lewis Dot Structure for **HPO_3^{2-}** and all possible resonance structures. Assign Formal Charges.
5. Draw the Lewis Dot Structure for **CHO_2^{1-}** and all possible resonance structures. Assign Formal Charges.
6. Draw the Resonance Hybrid Structure for **PO_4^{3-}**.
7. Draw the Resonance Hybrid Structure for **NO_3^-**.

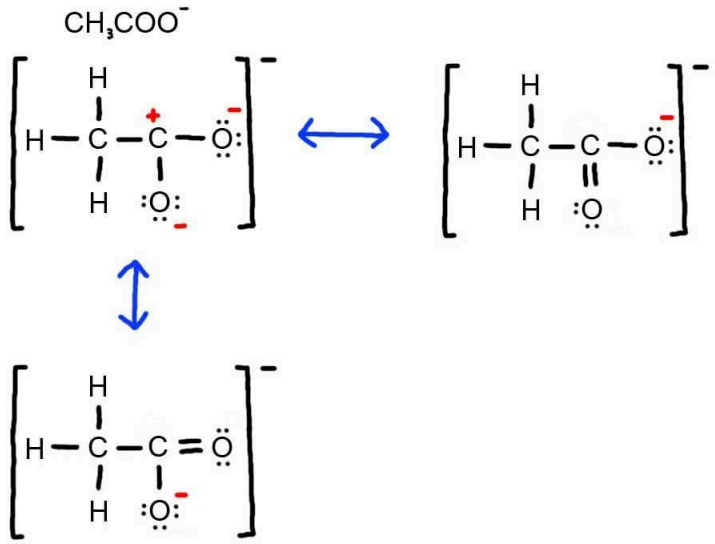
Numerical Answers

1. False, because the electrons were not moved around, only the atoms (this violates the Resonance Structure Rules).

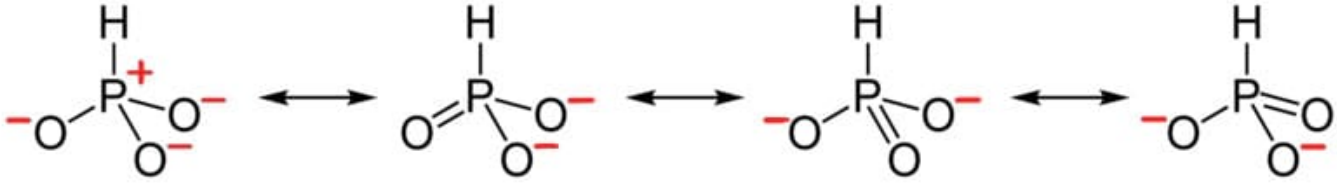
3. Below are the all Lewis dot structure with formal charges (in red) for Sulfate ($\mathbf{SO_4^{2-}}$). There isn't a most favorable resonance of the Sulfate ion because they are all identical in charge and there is no change in Electronegativity between the Oxygen atoms.



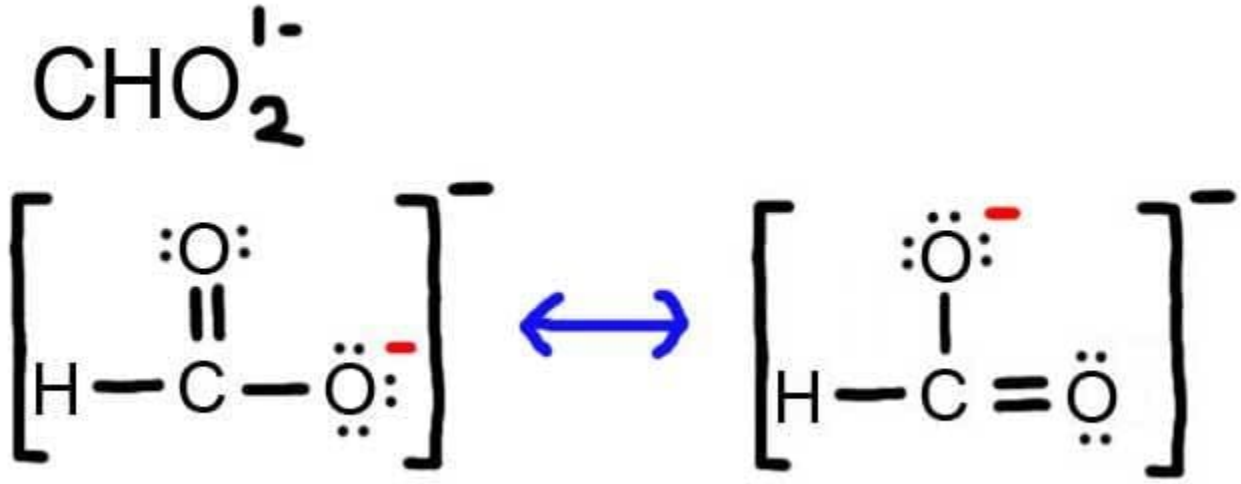
4. Below is the resonance for $\mathbf{CH_3COO^-}$, formal charges are displayed in red. The Lewis Structure with the most formal charges is not desirable, because we want the Lewis Structure with the least formal charge.



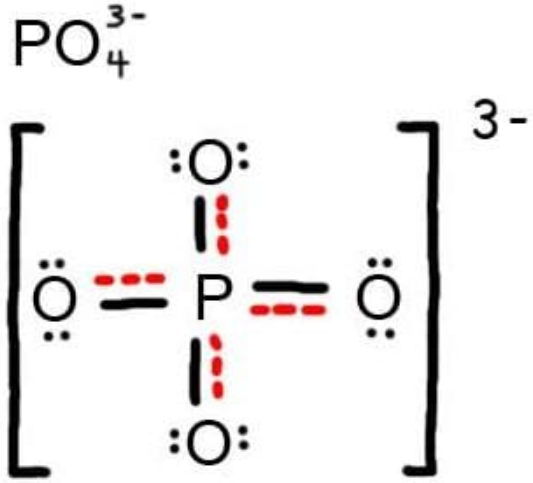
5. The resonance for $\mathbf{HPO_3^{2-}}$, and the formal charges (in red).



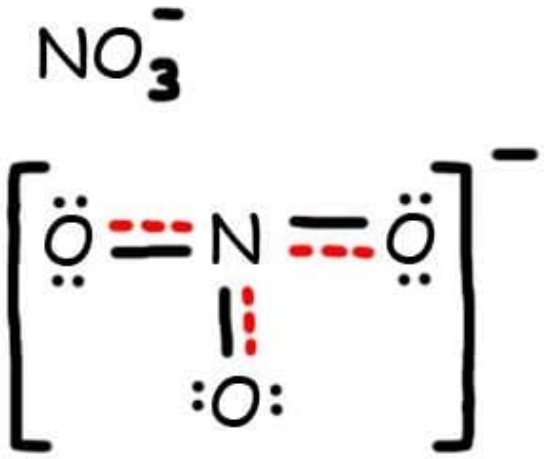
6. The resonance for **CHO_2^{1-}**, and the formal charges (in red).



7. The resonance hybrid for **PO_4^{3-}**, hybrid bonds are in red.



8. The resonance hybrid for **NO_3^-**, hybrid bonds are in red.



8.7: EXCEPTIONS TO THE OCTET RULE

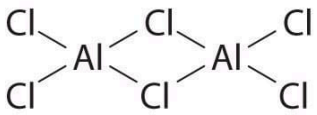
Conceptual Problems

1. What regions of the periodic table contain elements that frequently form molecules with an odd number of electrons? Explain your answer.
2. How can atoms expand their valence shell? What is the relationship between an expanded valence shell and the stability of an ion or a molecule?
3. What elements are known to form compounds with less than an octet of electrons? Why do electron-deficient compounds form?
4. List three elements that form compounds that do not obey the octet rule. Describe the factors that are responsible for the stability of these compounds.

Numerical Problems

1. What is the major weakness of the Lewis system in predicting the electron structures of PCl_6^- and other species containing atoms from period 3 and beyond?

2. The compound aluminum trichloride consists of Al_2Cl_6 molecules with the following structure (lone pairs of electrons removed for clarity):



   Does this structure satisfy the octet rule? What is the formal charge on each atom? Given the chemical similarity between aluminum and boron, what is a plausible explanation for the fact that aluminum trichloride forms a dimeric structure rather than the monomeric trigonal planar structure of BCl_3?

3. Draw Lewis electron structures for ClO_4^-, IF_5, $SeCl_4$, and SbF_5.

4. Draw Lewis electron structures for ICl_3, Cl_3PO, Cl_2SO, and AsF_6^-.

5. Draw plausible Lewis structures for the phosphate ion, including resonance structures. What is the formal charge on each

atom in your structures?

6. Draw an acceptable Lewis structure for PCl_5, a compound used in manufacturing a form of cellulose. What is the formal charge of the central atom? What is the oxidation number of the central atom?

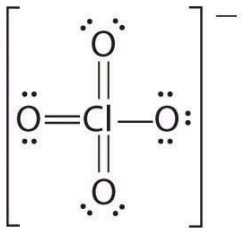
7. Using Lewis structures, draw all of the resonance structures for the BrO_3^- ion.

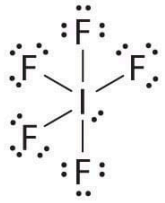
8. Draw an acceptable Lewis structure for xenon trioxide (XeO_3), including all resonance structures.

Numerical Answers

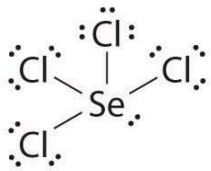
1.
2.

3. ClO_4^- (one of four equivalent resonance structures)

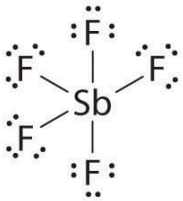




IF_5

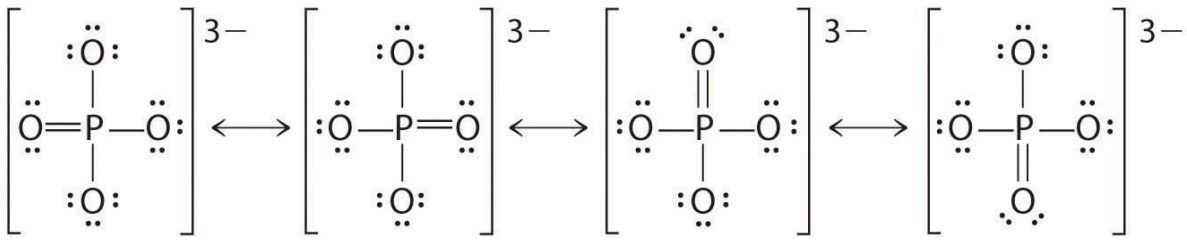


$SeCl_4$

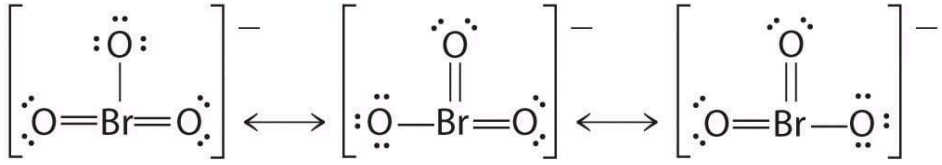


SbF_5

4.

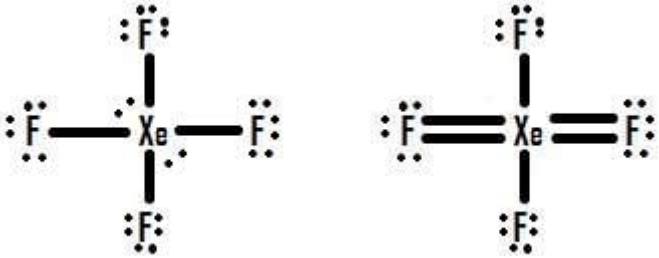
5. 

The formal charge on phosphorus is 0, while three oxygen atoms have a formal charge of –1 and one has a formal charge of zero.

6. 

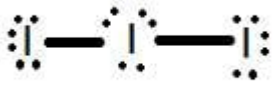
Practice Problems

1. Draw the Lewis structure for the molecule I_3^-.
2. Draw the molecule ClF_3.
3. The central atom for an expanded octet must have an atomic number larger than what?
4. Draw the Lewis structure for the molecule NO_2.
5. Which Lewis structure is more likely?

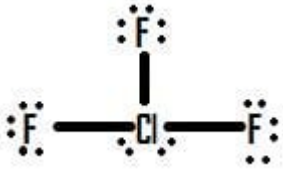


or

Practice Answers

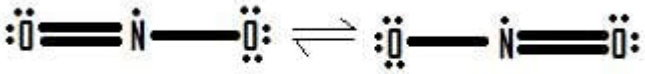


1.

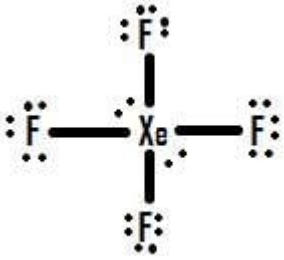


2.

3. 10 (Sodium and higher)



4.



5.

8.8: STRENGTHS OF COVALENT BONDS

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8.S: Basic Concepts of Chemical Bonding (Summary)

8.1: CHEMICAL BONDS, LEWIS SYMBOLS AND THE OCTET RULE

Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds. Lewis electron dot symbols, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of 8 valence electrons in their compounds.

- **Ionic bond**: bond formed on the basis of electrostatic forces that exist between oppositely charged ions. The ions are formed from atoms by transfer of one or more electrons
- **Covalent bond**: bond formed between two or more atoms by a sharing of electrons
- **Metallic bond**: bonding in which the bonding electrons are relatively free to move throughout the 3D structure
- **Electron dot symbols**: aka **Lewis symbols**; simple and convenient way of showing the valence electrons of atoms and keeping tack of them in the course of bond formation
- The number of valence electrons of any representative element is the same as the column number of the element in the periodic table
- **Octet rule**: atoms tend to lose or gain electrons until they are surrounded by 8 valence electrons

8.2: IONIC BONDING

The amount of energy needed to separate a gaseous ion pair is its bond energy. Forming ionic compounds is usually extremely exothermic. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance.

Energies of Ionic Bond Formation

The formation of ionic compounds is very exothermic

Removing an electron from an atom, such as Na, is endothermic because energy needs to be used to overcome the attractive forces within the atom. Adding an electron is the opposite process and releases lots of energy

The principal reason that ionic compounds are stable is the attraction between ions of unlike charge. This attraction draws the ions together, releasing energy and causing the ions to form a solid array (lattice)

Lattice energy: energy required to separate completely a mole of a solid ionic compounds into its gaseous ions

Large values of lattice energy mean that the ions are strongly attracted to one another

Energy released by the attraction between the ions of unlike charges more than makes up for the endothermic nature of ionization energies, making the formation of ionic compounds an exothermic process

$$E = k\frac{Q_1 Q_2}{d}$$

- E = potential energy of two interacting charged particles
- Q_1 and Q_2 = charges on the particles
- D= distance between the particles
- K = constant; 8.99 X 10^9 Jm/C^2

For a given arrangement of ions, the lattice energy increases as the charges of ions increase and as their radii decrease. The magnitude of lattice energies depends primarily on the ionic charges because ionic radii do not vary over a wide range.

Electron Configurations of Ions

Many ions tend to have noble gas electron configurations. This is why Na can have a +1 charge, but not a +2 one. Once an ion has reached noble gas configuration, it wants to stay there.

- Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$ = [Ne] $3s^1$
- Na^+: $1s^2\ 2s^2\ 2p^6$ = [Ne]
- Na^{2+}: $1s^2\ 2s^2\ 2p^5$

Similarly, addition of electrons to nonmetals is either exothermic or slightly endothermic as long as electrons are being added to the valence shell. Further addition of electrons requires tremendous amounts of energy; more than is available form the lattice energy

- Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ = [Ne] $3s^2\ 3p^5$
- Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ = [Ar]
- Cl^2: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ = [Ar]

The lattice energies of ionic compounds are generally large enough to compensate for the loss of up to only 3 electrons from atoms. Thus we find cations only having charges of +1, +2, or +3.

Because most transition metals have more than 3 electrons beyond a noble gas core, attainment of a noble gas configuration for these ions is usually impossible.

When a positive ion is formed from an atom, electrons are always lost first from the subshell with the largest value of *n*. Thus, a transition metal always loses the outer *s* electrons before it loses electrons from the underlying *d* subshell.

8.3 Sizes of Ions

Sizes of ions are important in determining both the way in which the ions pack in a solid and the lattice energy of the solid. It is also a major factor governing the properties of ions in solution

The size of an atom depends on its nuclear charge, the number of electrons it possesses, and the orbitals in which the outer-shell electrons reside

Positive ions are formed by removing 1 or more electrons from the outermost region of the atom. Thus, the formation of a cation not only vacates the most spatially extended orbitals, it also decreases the total electron-electron repulsions. Hence, cations are smaller than the original atoms from which they came.

The opposite happens when speaking of negative ions. An added electron increases electron-electron repulsions and causes the electrons to spread out more in space.

For ions of the same charge, size increases as we go down a group

8.3: COVALENT BONDING

The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms. Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest.

Ionic substances are usually brittle with high melting points. They are usually crystalline, meaning that they have flat surfaces that make characteristic angles with one another.

- **Covalent bond**: chemical bond formed by sharing a pair of electrons
- **Lewis structure**: structure that represents bonding using dots for unpaired electrons and lines for bonds

For nonmetals, the number of valence electrons is the same as the group number

Knowing this, we can predict that an element in Group 7A would need one covalent bond in order to get an octet, an element in Group 6A would need two, and so on.

Multiple Bonds

- **Single bond**: sharing of one pair of electrons, one covalent bond
- **Double bond**: two shared electrons

Distance between bonded atoms decreases as the number of shared electron pairs increases

8.4: BOND POLARITY AND ELECRONEGATIVITY

Bond polarity and ionic character increase with an increasing difference in electronegativity. The electronegativity (χ) of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average

- **Bond polarity**: measure of how equally the electrons are shared between the atoms in a chemical bond
- **Nonpolar bond**: one in which the electrons are shared equally between the two atoms
- **Polar covalent bond**: one of the atoms exerts a greater attraction for the electron than the other

Electronegativity

Used to estimate whether a bond will be nonpolar, polar covalent, or ionic

Electronegativity: ability of an atom *in a molecule* to attract electrons to itself

An atom with a very negative electron affinity and high ionization energy will both attract electrons from other atoms and resist having its electrons attracted away; it will be highly electronegative

Highest electronegativity = 4.0 (Fluorine), lowest = 0.7 (Cesium)

Electronegativity increases form left to right, and usually decreases with increasing atomic number in any one group

Electronegativity and Bond Polarity

Differences in electronegativities:

Nonpolar = 0 – 0.4

Polar covalent = 0.4 – 1.6

Ionic = > 1.6 (> 50% = ionic)

δ^+ and δ : "delta sign"; represent partial positive and negative charge. The atom with the δ is the more electronegative one

8.5: DRAWING LEWIS STRUCTURES

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families.

1. Sum the valence electrons from all atoms. For an anion, add an electron to the total negative charge. For a cation, subtract an electron.
2. Write the symbols for the atoms to show which atoms are attached to which, and connect them with a single bond.
3. Complete the octets of the atoms bonded to the central atom.
4. Place any leftover electrons on the central atom, even if doing so results in more than an octet

5. If there are not enough electrons to give the central atom an octet, try multiple bonds

8.6: RESONANCE STRUCTURES

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a double-headed arrow between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures.

Resonance structures (resonance forms) are individual Lewis structures in cases where two or more Lewis structures are equally good descriptions of a single molecule. If a molecule (or ion) has two or more resonance structures, the molecule is a blend of these structures. The molecule *does* **not** oscillate rapidly between two or more different forms.

8.7: EXCEPTIONS TO THE OCTET RULE

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an odd number of valence electrons, (2) When there are too few valence electrons, and (3) when there are too many valence electrons

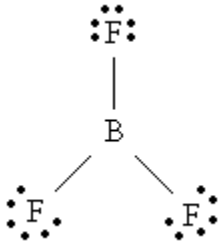
1. Molecules with an odd number of electrons
2. Molecules in which an atom has less than an octet
3. Molecules in which an atom has more than an octet

Odd Number of Electrons

In a few molecules, such as ClO_2, NO, and NO_2, the number of electrons is odd. In NO for example, there are 5+6 = 11 valence electron. Hence, complete pairing of these electrons is impossible and an octet around each atom cannot be achieved.

Less Than an Octet

Second type of exception occurs when there are fewer than eight electrons around an atom in a molecule or ion. Relatively rare situation; most often encountered in compounds of Boron and Beryllium. For example, let's consider Boron Trifluoride, BF_3



There are 6 electrons around the Boron atom. We can form a double bond between Boron and any of the 3 Fluorine atoms (3 possible resonance structures)

However, by doing so, we forced a Fluorine atom to share additional electrons with Boron. This would make the F atom to have a +1 charge, and the Boron atom to have a –1 charge, which is extremely unfavorable.

We then conclude that the structures containing the double bonds are less important than the one illustrated on the right. *Since in this case Boron has only 6 valence electrons, it will react violently with molecules that have an unshared pair of electrons.*

More Than an Octet

The octet rule works as well as it does because the representative elements usually employ only an *ns* and three *np* valence shell orbitals in bonding, and these hold eight electrons.

Because elements of the second period have only 2s and 2p orbitals, they cannot have more than an octet of electrons in their valence shells. However, from the third period on, the elements have unfilled *nd* orbitals that can be used in bonding.

Size also plays an important role in determining whether an atom can accommodate more than eight electrons. The larger the central atom, the larger the number of atoms that can surround it. The size of the surrounding atoms is also important. Expanded valence shells occur most often when the central atom is bonded to the smallest and most electronegative atoms.

8.8: STRENGTHS OF COVALENT BONDS

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. The bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms.

Bonddissociation energy: aka **bond energy**; enthalpy change, ΔH, required to break a particular bond in a mole of gaseous substance.

For polyatomic molecules, we must often utilize average bond energies.

Bond energy is *always* positive, the greater the bond energy, the stronger the bond

A molecule with strong bonds generally has less tendency to undergo chemical change than does one with weak bonds

Bond Energies and the Enthalpy of Reactions

$\Delta H = \Sigma$ (bond energies of bonds broken) – Σ (bond energies of bonds formed)

If $\Delta H > 0$, the reaction is endothermic

If $\Delta H < 0$, the reaction is exothermic

$Cl - Cl_{(g)} + H - CH_{3\,(g)} \rightarrow H - Cl_{(g)} + Cl - CH_{3\,(g)}$

Bonds broken: 1 mol Cl – Cl, 1 mol C – H

Bonds made: 1 mol H – Cl, 1 mol C – Cl

$$\Delta H = [D(Cl–Cl) + D(C–H)][D(H–Cl) + D(Cl–Cl)]$$

= (242 kJ + 413 kJ) – (431kJ + 328 kJ)

= 104 kJ

Bond Strength and Bond Length

As the number of bonds between a given element increase, the bond energy increases and the bond length decreases. Hence, the atoms are held more tightly and closely together. In general, *as the number of bonds between two atoms increases, the bond grows shorter and stronger.*

8.10 Oxidation Numbers

Oxidation Numbers: aka **Oxidation states**; a positive or negative whole number assigned to an element in a molecule or ion on the basis of a set of normal rules; to some degree it reflects the positive or negative character of an atom

Oxidation numbers do NOT correspond to real charges on the atoms, EXCEPT in the special case of simple ionic substances

1. *The oxidation form of an element in its elemental form is zero.*
2. *The oxidation number of a monoatomic ion is the same as its charge.* For example, the oxidation number of sodium in Na^+ is +1, and that of sulfur in S^2 is –2

3. *In binary compounds (those with two different elements), the element with greater electronegativity is assigned a negative oxidation number equal to its charge in simple ionic compounds the element*. For example, consider the oxidation state of Cl in PCl_3. Cl is more electronegative than P. In its simple ionic compounds, Cl appears as the ion Cl. Thus, in PCl_3, Cl is assigned an oxidation number of –1.
4. *The sum of the oxidation numbers equals zero for an electrically neutral compound and equals the overall charge of the ionic species*. For example, PCl_3 is a neutral molecule. Thus, the sum of oxidation number of the P and Cl atoms must equal zero Because the oxidation number of each Cl in this compound is –1 (rule 3), the oxidation number of P must be +3.

Group 1A elements are +1, Group 2A elements are +2, and Aluminum is +3.

The most electronegative element, F, is always found in the –1 oxidation state. Oxygen is usually in the –2 state, however, it can be –1 in peroxides.

Hydrogen has an oxidation number of +1 when it is bonded to a more electronegative element (most nonmetals), and of –1 when bonded to less electronegative elements (most metals)

Oxidation Numbers and Nomenclature

Name of the less electronegative element is given first, followed by the name of the more electronegative element modified to have an *–ide* ending

Compounds of metals in higher oxidation states tend to be molecular rather than ionic

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9: MOLECULAR GEOMETRY AND BONDING THEORIES

9.1: Molecular Shapes

9.2: The VSEPR Model

9.3: Molecular Shape and Molecular Polarity

9.4: Covalent Bonding and Orbital Overlap

9.5: Hybrid Orbitals

9.6: Multiple Bonds

9.7: Molecular Orbitals

9.8: Second-Row Diatomic Molecules

9.E: Exercises

9.S: Molecular Geometry and Bonding Theories (Summary)

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9.1: Molecular Shapes

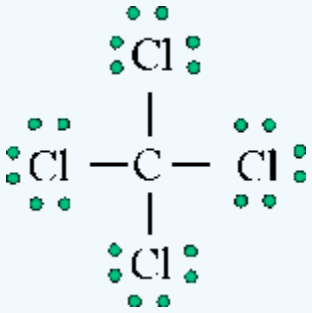
The Lewis electron-pair approach described previously can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however.

Molecular Geometry

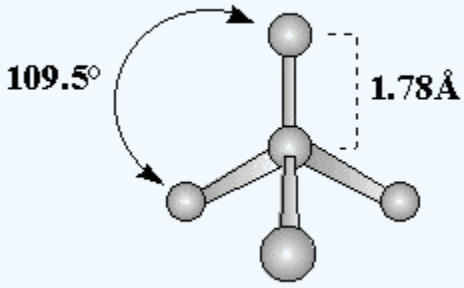
The specific three dimensional arrangement of atoms in molecules is referred to as **molecular geometry**. We also define molecular geometry as the positions of the atomic nuclei in a molecule. There are various instrumental techniques such as X-Ray crystallography and other experimental techniques which can be used to tell us where the atoms are located in a molecule. Using advanced techniques, very complicated structures for proteins, enzymes, DNA, and RNA have been determined. Molecular geometry is associated with the chemistry of vision, smell, taste, drug reactions, and enzyme controlled reactions to name a few.

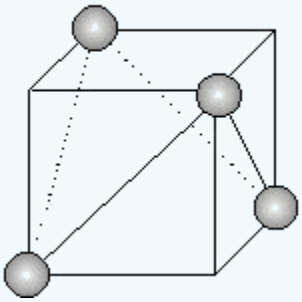
Example $9.1.1$: Carbon Tetrachloride

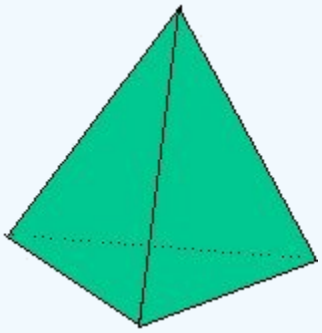
The Lewis structure of carbon tetrachloride provides information about connectivities, provides information about valence orbitals, and provides information about bond character.



However, the Lewis structure provides no information about the shape of the molecule, which is defined by t*he bond angles and the bond lengths*. For carbon tetrachloride, each C-Cl bond length is 1.78Å and each Cl-C-Cl bond angle is 109.5°. Hence, carbon tetrachloride is ***tetrahedral*** in structure:





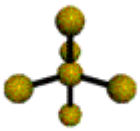
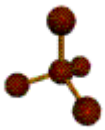
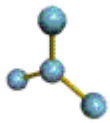
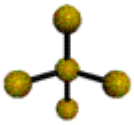
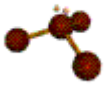
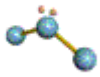
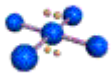
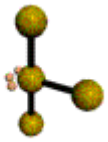


Molecular Geometries of AB_n molecules

Molecular geometry is associated with the specific orientation of bonding atoms. A careful analysis of electron distributions in orbitals will usually result in correct molecular geometry determinations. In addition, the simple writing of Lewis diagrams can also provide important clues for the determination of molecular geometry. Molecular shapes, or geometries, are critical to molecular recognition and function. Table $9.1.1$ shows some examples of geometries where a central atom A is bonded to two or

more X atoms. As indicated in several of the geometries below, non-bonding electrons E can strongly influence the molecular geometry of the molecule.

Table 9.1.1*:*

6	5	4	3	2
AX_6  octahedral	AX_5  trigonal bipyramidal	AX_4  tetrahedral	AX_3  trigonal planar	AX_2 Linear linear
1 lone pair of electrons				
AX_5E  square pyramidal	AX_4E  distorted tetrahedron	AX_3E  pyramidal	AX_2E  nonlinear	AXE Linear linear
2 lone pairs of electrons				
AX_4E_2  square planar	AX_3E_2  T-shaped	AX_2E_2  bent	AXE_2 Linear linear	

These structures can generally be predicted, when A is a nonmetal, using the "valence-shell electron-pair repulsion model (VSEPR) discussed in the next section.

Contributors and Attributions

- Mike Blaber (Florida State University)

- Robyn Rindge (Class of '98) who now works for PDI Dreamworks (look for his name in the credits of Shrek2.). Robyn drew these rotating molecules using Infini-D (MetaCreations).
- Paul Groves, chemistry teacher at South Pasadena High School and Chemmy Bear(opens in new window)

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9.2: The VSEPR Model

Learning Objectives

- To use the VSEPR model to predict molecular geometries.
- To predict whether a molecule has a dipole moment.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion** (VSEPR) model (pronounced "vesper"), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

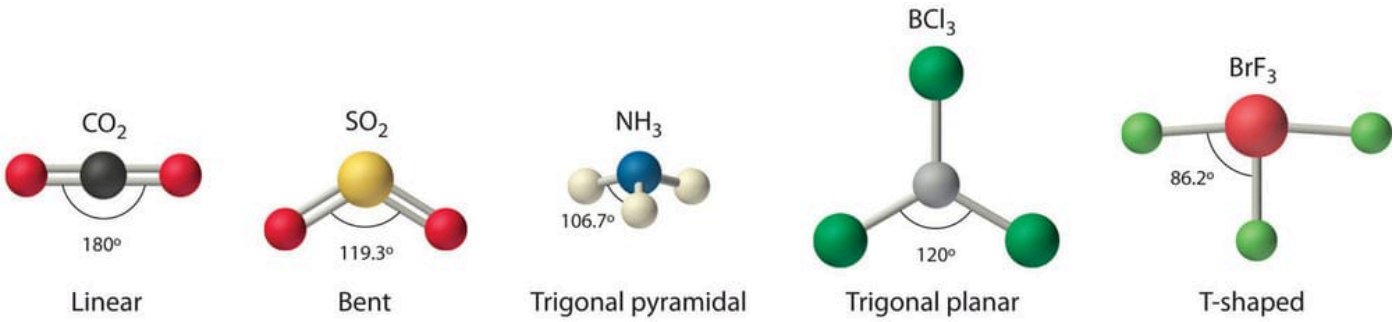


Figure 9.2.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figures 9.2.1 and 9.2.2.

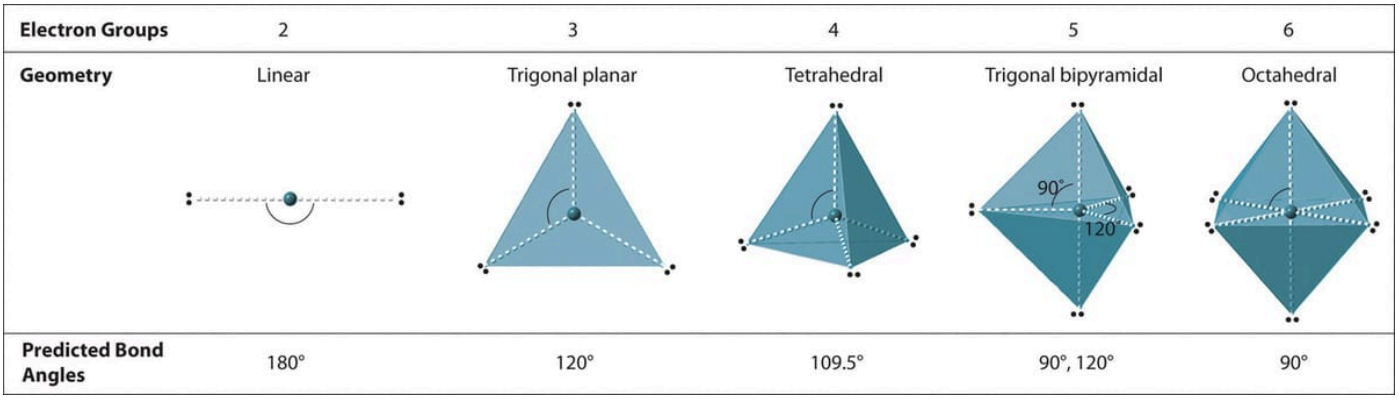


Figure 9.2.2: Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions. (CC BY-NC-SA; anonymous)

In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles. Using this information, we can describe the molecular geometry, the arrangement of the *bonded atoms* in a molecule or polyatomic ion.

VESPR Produce to predict Molecular geometry

This VESPR procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure 9.2.2 and Figure 9.2.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

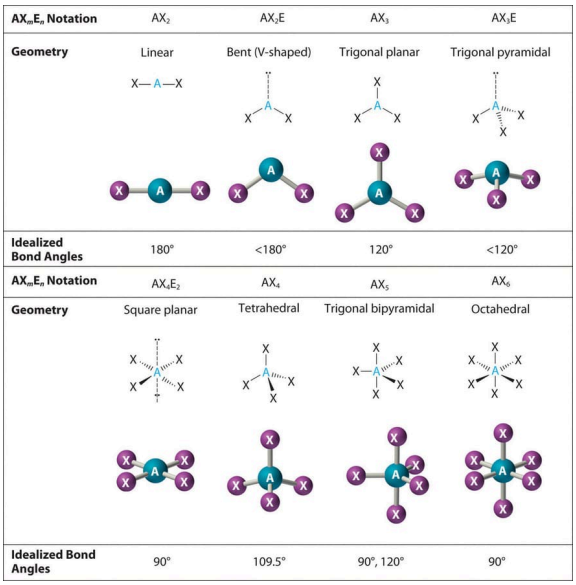


Figure 9.2.3: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line. (CC BY-NC-SA; anonymous)

Linear, bent, trigonal planar, trigonal pyramidal, square planar, tetrahedral, trigonal bipyramidal, octahedral.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2 Molecules: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

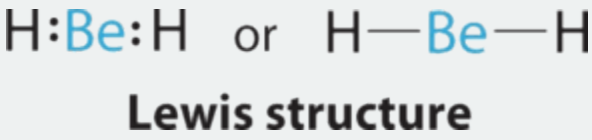


Figure 9.2.2 that the arrangement that minimizes repulsions places the groups 180° apart. (CC BY-NC-SA; anonymous)

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 9.2.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2 Molecules: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

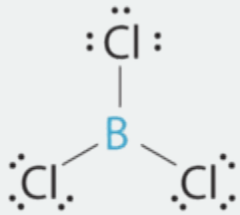
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 9.2.3). The structure of CO_2 is shown in Figure 9.2.1.

Three Electron Groups

AX_3 Molecules: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

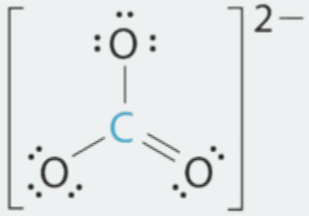
Figure 9.2.2): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 9.2.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 9.2.2.

AX_3 Molecules: CO_3^{2-}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as



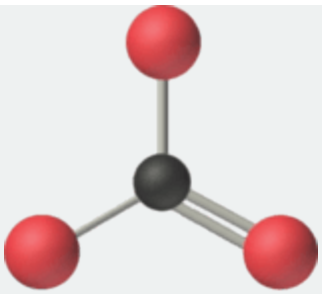
Lewis structure

Figure 9.2.2).

The three oxygens are arranged in a triangular shape with carbon at the center. Two of the oxygens have three lone pairs. One ocht oxygens has 2 lone pairs and is double bonded to the carbon. The molecule has a minus 2 charge.

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure 9.2.3 that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.



Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E Molecules: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.

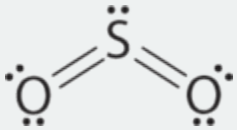


Figure 9.2.2): (CC BY-NC-SA; anonymous)

The two oxygens are double bonded to the sulfur. The oxygens have 2 lone pairs while sulfur had one lone pair.

3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 9.2.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures 9.2.2 and 9.2.3). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

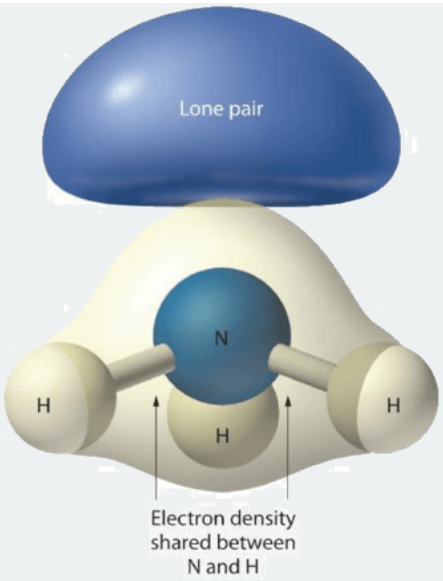
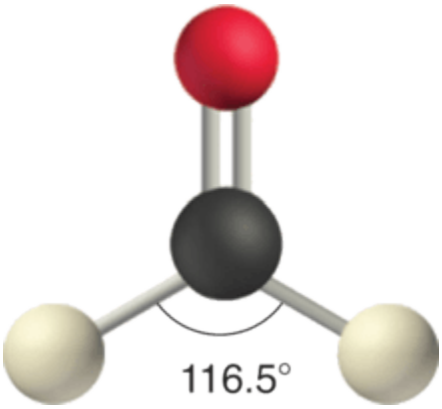


Figure 9.2.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair. (CC BY-NC-SA; anonymous)

As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

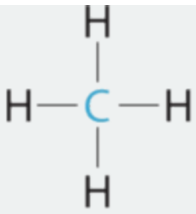


Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4 Molecules: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

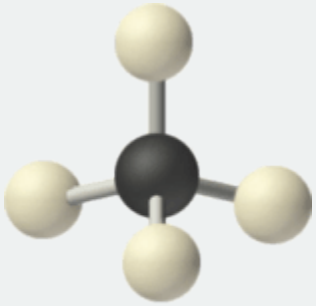


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 9.2.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

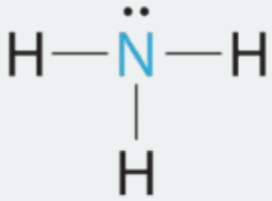
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 9.2.3).



Molecular geometry
(tetrahedral)

AX_3E Molecules: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 9.2.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 9.2.3 and Figure 9.2.4).

AX_2E_2 Molecules: H_2O

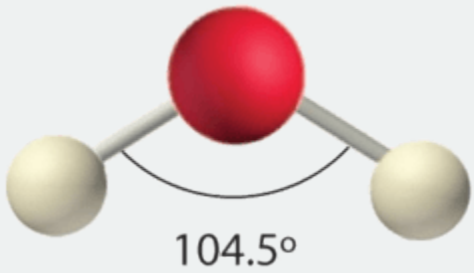
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



Figure 9.2.2: (CC BY-NC-SA; anonymous)

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.



Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5 Molecules: PCl_5

1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is

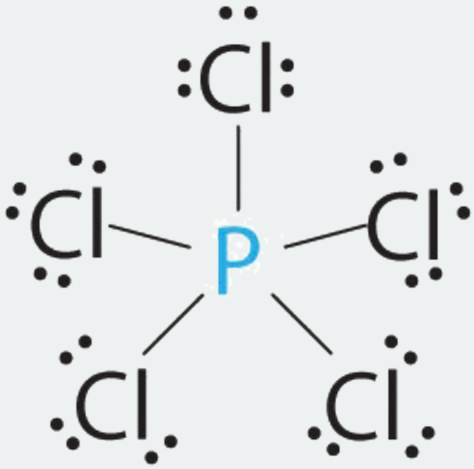
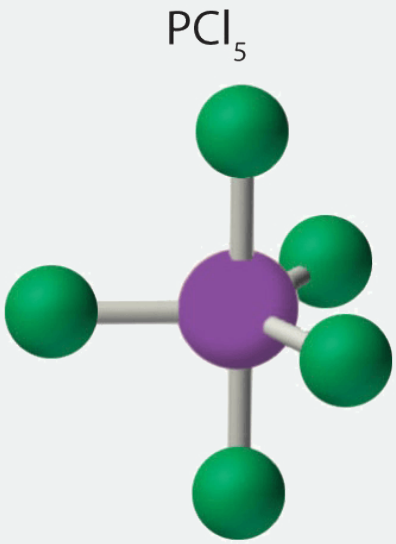


Figure 9.2.2): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 9.2.3. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



AX_4E Molecules: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

Four fluorenes are bonded to a central sulfur. Each fluorine has three lone pairs. Sulfur has one lone pair.

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 9.2.2.

3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the axial position, we have three LP–BP repulsions at 90°. If we place it in the equatorial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the *equatorial position is more stable than the one with the lone pair in the axial position*. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

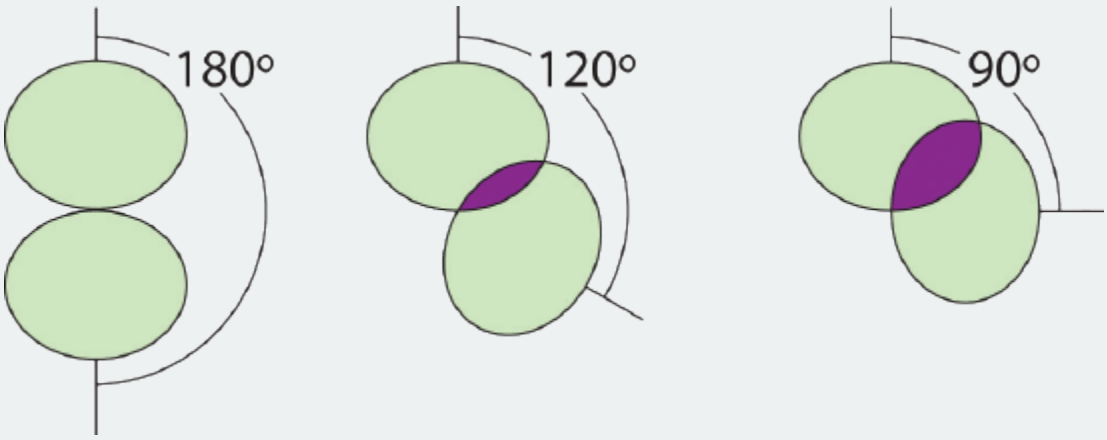
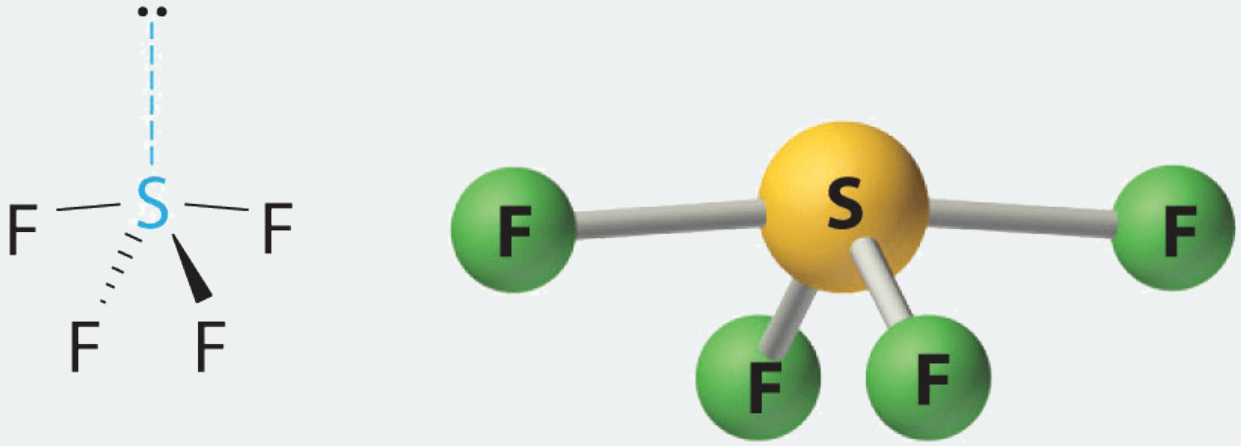


Figure 9.2.5: Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

180 degree angle has no shared space between teo electron pair, 120 degree angle has some shared area between two electron pairs. 90 degree angle has more shared space than 120.

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

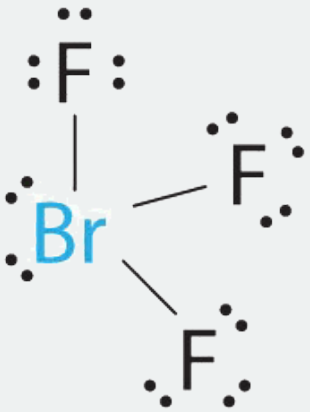
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2 Molecules: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



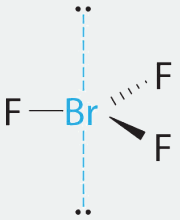
Lewis structure

Three fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has two lone pairs.

Once again, we have a compound that is an exception to the octet rule.

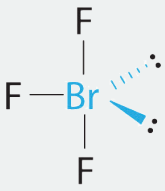
2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



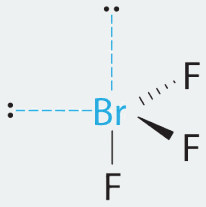
Lone pairs axial

(a)



Lone pairs equatorial

(b)



Lone pairs axial and equatorial

(c)

Interactions

90° LP–LP	0	0	1
90° LP–BP	6	4	3

If the lone pairs are axiam, the 90 degree LP-LP interactions are o and the 90 degree LP-BP interaction is zero. If the Lone pares are equatorial there are zero 90 degree LP-LP interactions and four 90 degree LP-BP intereactions. If the lone pairs are axial and equatorial there is one 90 degree LP-LP interaction and three 90 degree LP-BP interaction.

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions (Figure 9.2.2.1).

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

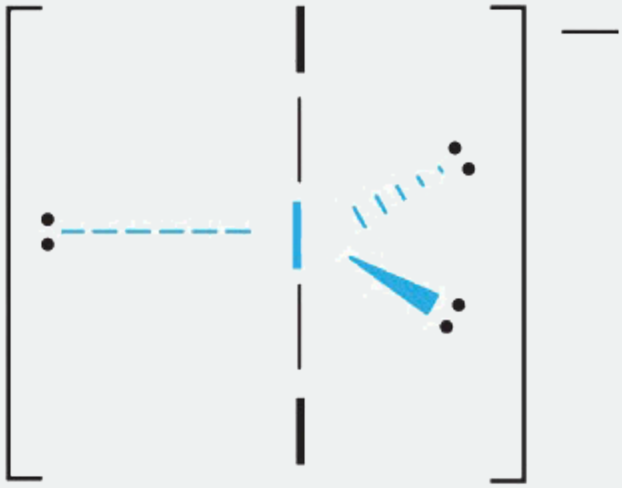
AX_2E_3 Molecules: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



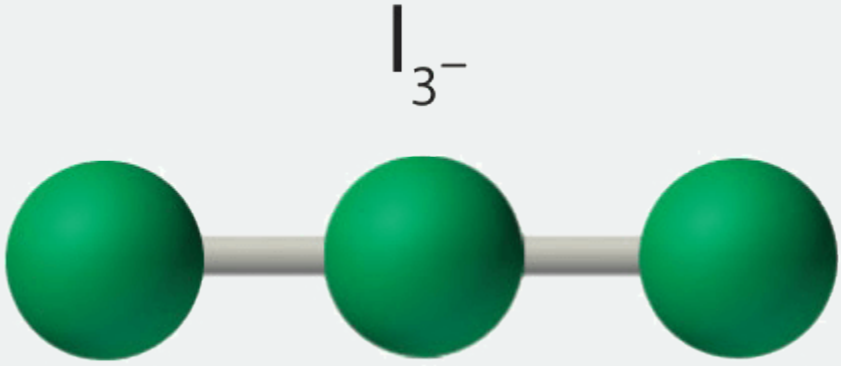
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

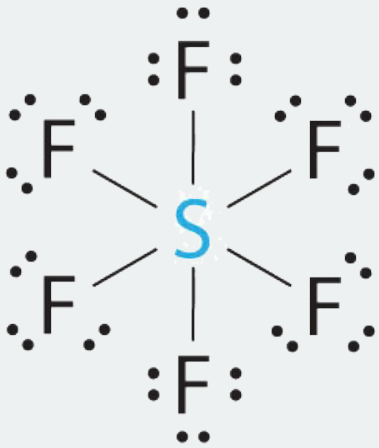


Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 9.2.2.)

AX_6 Molecules: SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



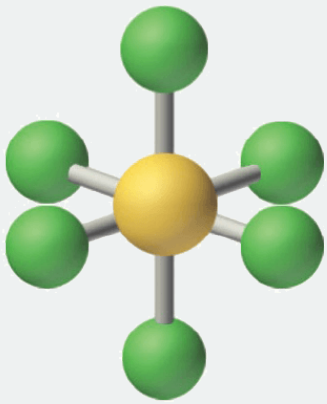
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure $9.2.2$ that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

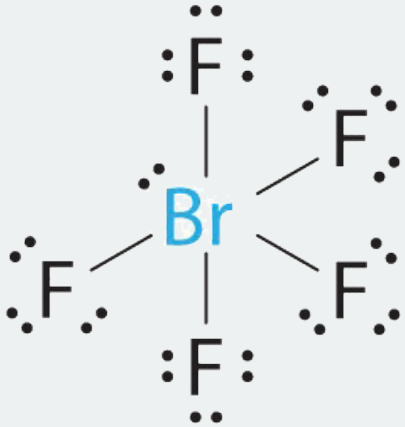
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX_5E Molecules: BrF_5

1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is

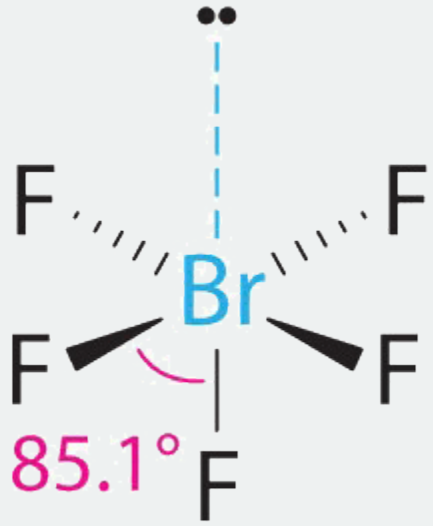


Lewis structure

Five fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has one lone pair.

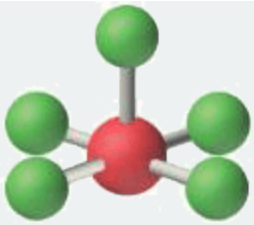
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

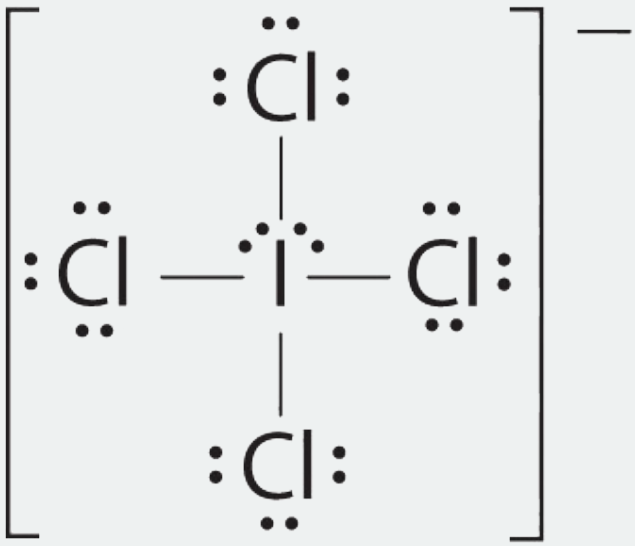
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is s*quare pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



Molecular geometry
(square pyramidal)

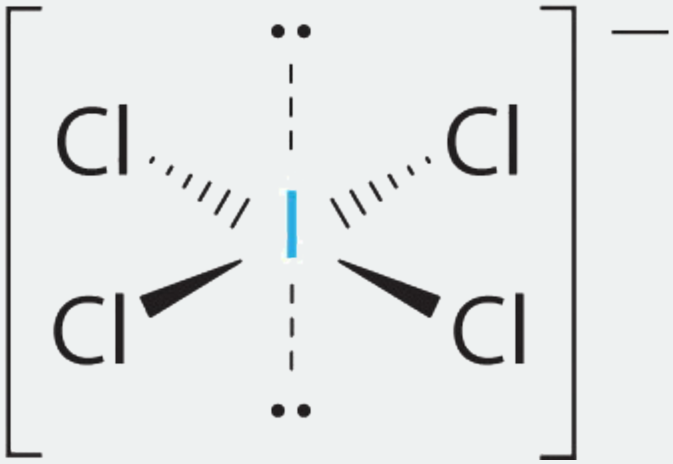
AX_4E_2 Molecules: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



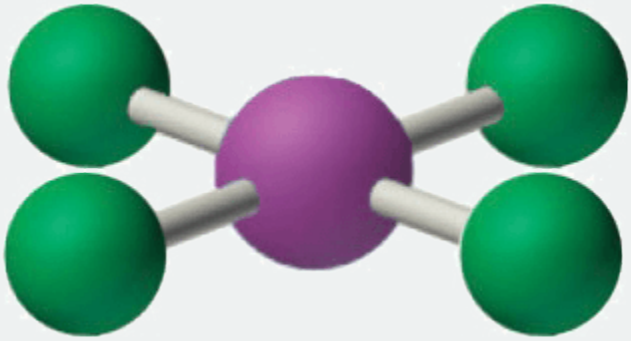
Four chlorines are bonded to a central iodine. Each chlorine has three electron pairs. The iodine has two electron pairs. The molecule is negatively charged.

2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl4– ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure $9.2.6$.

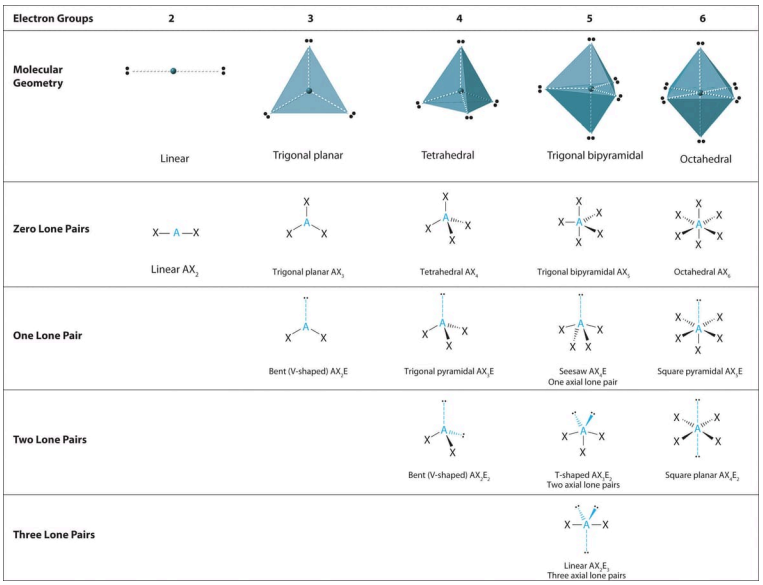


Figure 9.2.6***:*** *Overview of Molecular Geometries*

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Example 9.2.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A. Draw the Lewis electron structure of the molecule or polyatomic ion.
B. Determine the electron group arrangement around the central atom that minimizes repulsions.
C. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.
D. Describe the molecular geometry.

Solution:

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is

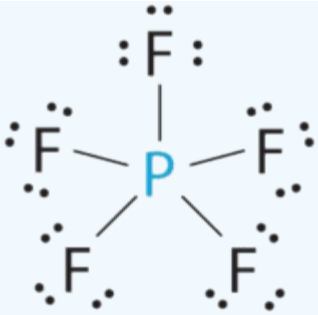


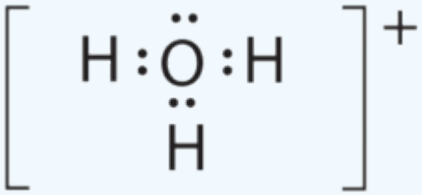
Figure 9.2.6): (CC BY-NC-SA; anonymous)

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is

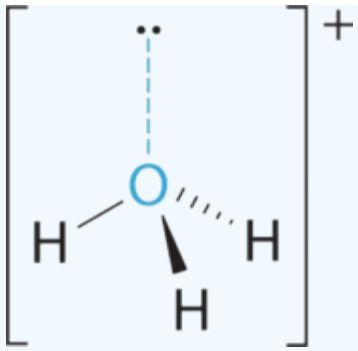


Three hydrogens are bonded to a central oxygen. The oxygen has two lone pairs. The molecule has a charge of plus one.

B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



Exercise 9.2.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer a available at the end of this section.

Example 9.2.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example 9.2.1.

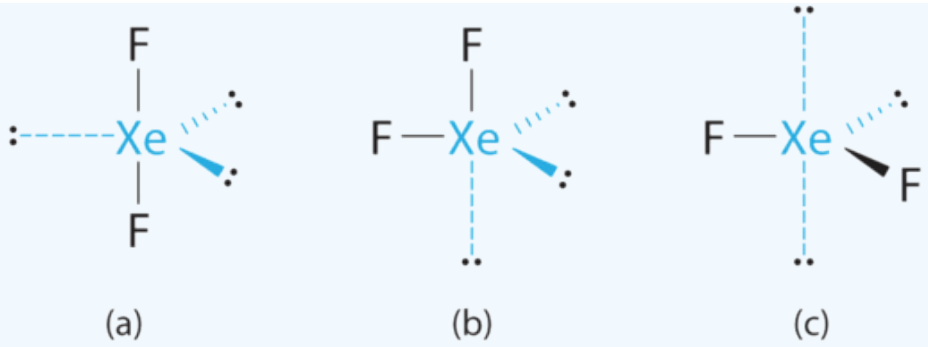
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



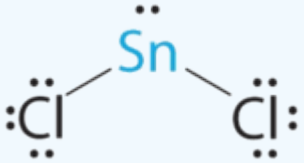
Interactions			
90 LP–LP	0	2	2

If the two F atoms are axial ther are zero 90 LP-LP interactions. If the two F atoms are axial and equatorial or just equatorial, there are 2 90 LP-LP interactions.

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



Two chlorines are bonded to a central tin. Each chlorine has three lone pairs. Tin has one lone pair.

B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise 9.2.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a available at the end of this section.

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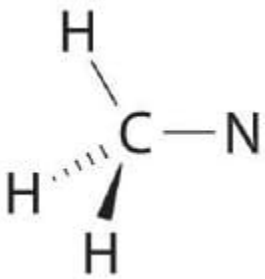
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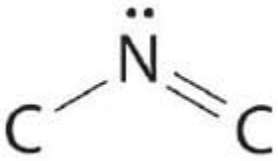
Molecules with No Single Central Atom

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4. We can therefore predict the CH_3–N portion of the molecule to be roughly tetrahedral, similar to methane:



The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



One carbon bonded to nitrogen and another carbon double bonded to the nitrogen. The nitrogen has one lone pair.

Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:

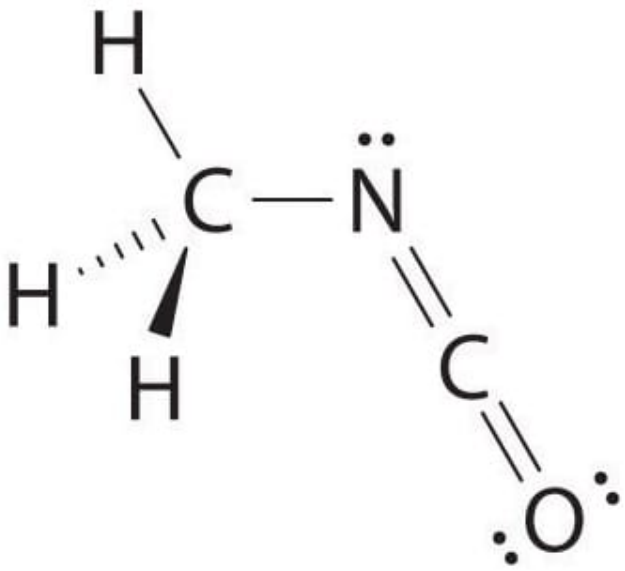


Figure 9.2.7).

Three hydrogens are bonded to a carbon. The carbon is also bonded to a nitrogen. The nitrogen is double bonded to another carbon. The second carbon is double bonded to an oxygen. The nitrogen has one lone pair. The oxygen has two lone pairs.

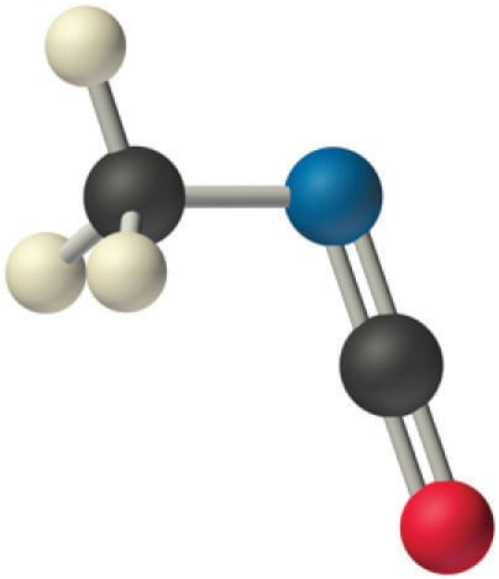


Figure 9.2.7: The Experimentally Determined Structure of Methyl Isocyanate

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

Example 9.2.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C{\equiv}CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 9.2.3 to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

Exercise 9.2.3

Predict the geometry of allene ($H_2C{=}C{=}CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer available at the end of this section.

Molecular Dipole Moments

You previously learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (Figure 9.2.8*a*). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (Figure 9.2.8*b*); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

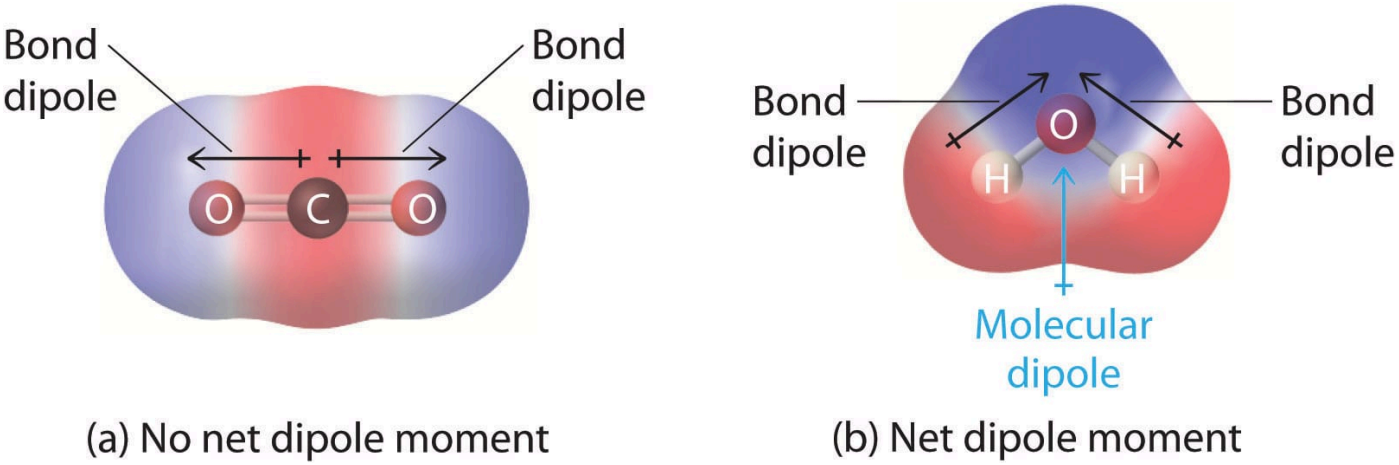


Figure 9.2.8: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.

Other examples of molecules with polar bonds are shown in Figure 9.2.9. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely

cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment. Molecules with asymmetrical charge distributions have a net dipole moment.

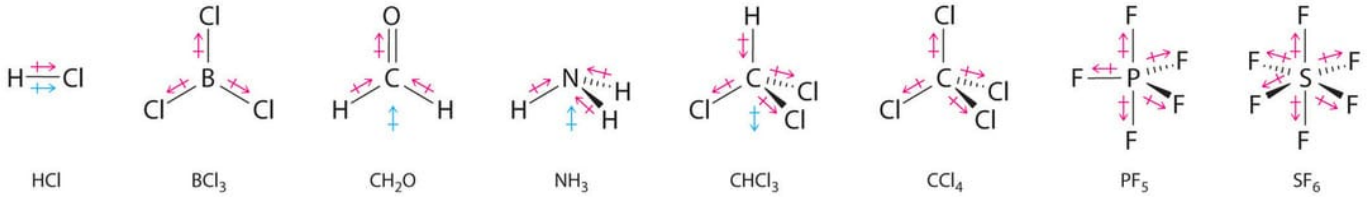


Figure 9.2.9: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

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Example 9.2.4

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

Given: three chemical compounds

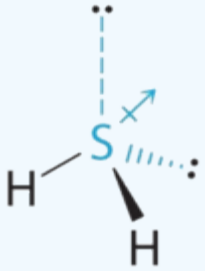
Asked for: net dipole moment

Strategy:

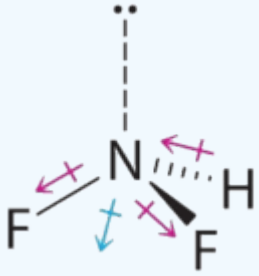
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

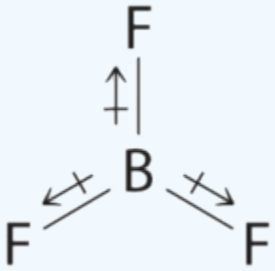
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 9.2.6). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



2. Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.



3. The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:



Exercise 9.2.4

Which molecule(s) has a net dipole moment?

- CH_3Cl
- SO_3
- XeO_3

Answer available at the end of this section.

Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers.

Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds. A combination of VSEPR and a bonding model, such as Lewis electron structures, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

Answers

Exercise 9.2.1

trigonal pyramidal

octahedral

linear

Exercise 9.2.2

trigonal planar

square planar

Exercise 9.2.3

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

Exercise 9.2.4

CH_3Cl and XeO_3

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9.3: Molecular Shape and Molecular Polarity

Learning Objectives

- To calculate the percent ionic character of a covalent polar bond

Previously, we described the two idealized extremes of chemical bonding:

- **ionic bonding**—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and
- **covalent bonding**, in which electrons are shared *equally* between two atoms.

Most compounds, however, have polar covalent bonds, which means that electrons are shared *unequally* between the bonded atoms. Figure $9.3.1$ compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a *polar bond*.

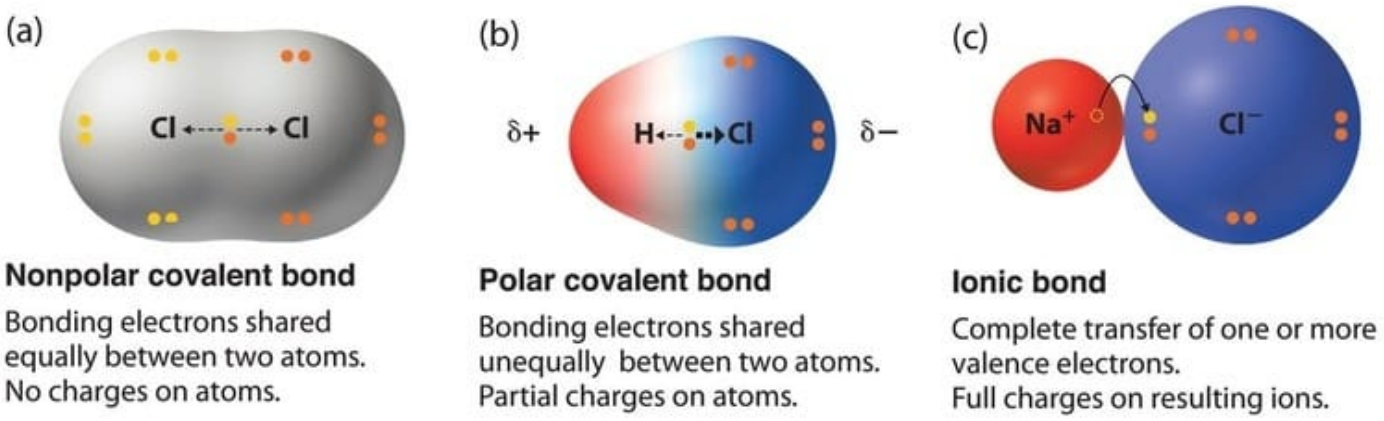


Figure $9.3.1$: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. *Electronegativity* (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{less\ electronegative}{A}} - \underset{\delta^-}{\overset{more\ electronegative}{B}} \tag{9.3.1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms:

$$\Delta\chi = \chi_B - \chi_A.$$

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms (Table A2): $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta+}{H} \quad - \quad \overset{\delta-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

> Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in $NaCl$, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a dipole moment where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr \tag{9.3.2}$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m \tag{9.3.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 9.3.2).

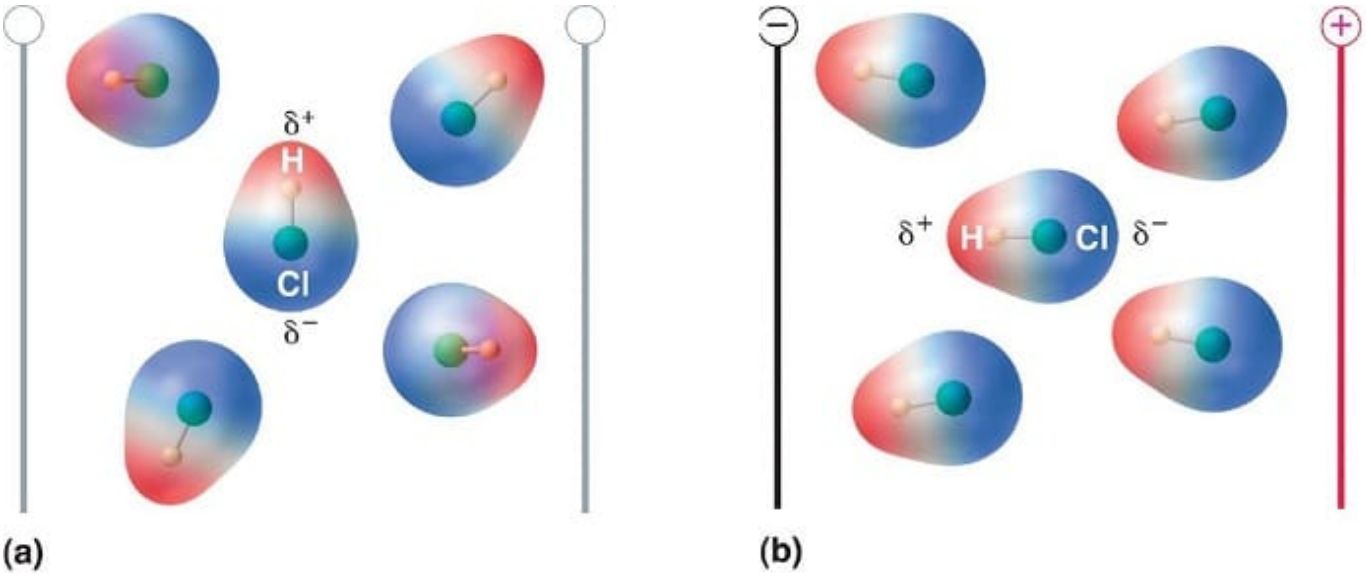


Figure 9.3.2: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), theHClmolecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 9.3.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full –1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 1.109 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{127.8\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) \\ &= 2.901 \times 10^{-20}\ C \end{aligned}$$

By dividing this calculated value by the charge on a single electron (1.6022 × 10^{-19} C), we find that the electron distribution inHCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about –0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} = 0.1811\ e^- \tag{9.3.4}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta^+}{H} \quad - \quad \overset{\delta^-}{Cl}$$

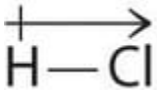
we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta^+}{H} \quad - \quad \overset{0.18\delta^-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine ($\chi_H = 2.20$ and $\chi_{Cl} = 3.16$) so

$$\chi_{Cl} - \chi_H = 0.96$$

This is a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule.Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

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A warning about Dipole Moment arrows

As the figure above shows, we represent dipole moments by an arrow with a length proportional to μ and pointing from the positive charge to the negative charge. However, the **opposite** convention is still widely used especially among physicists.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure $9.3.2$ shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as $NaCl_{(g)}$ and $CsF_{(g)}$ is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure $9.3.2$ show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example $9.3.1$.

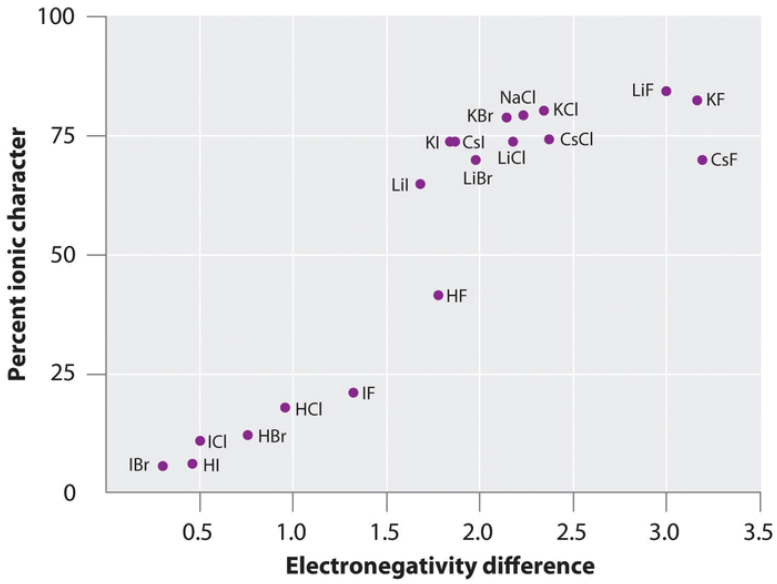


Figure $9.3.2$: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms. In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example $9.3.1$: percent ionic character

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A. Compute the charge on each atom using the information given and Equation 9.3.2
B. Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) \\ &= 1.272 \times 10^{-19}\ C \end{aligned}$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\begin{aligned} \text{ionic character} &= \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) \\ &= 79.39\% \simeq 79\% \end{aligned}$$

Exercise 9.3.1

In the gas phase, silver chloride ($AgCl$) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer available at the end of this section.

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity.

$$\mu = Qr$$

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 9.3.1

55.5%

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9.4: Covalent Bonding and Orbital Overlap

Learning Objectives

- To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of H_2O and NH_3, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including SrF_2 and BaF_2, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

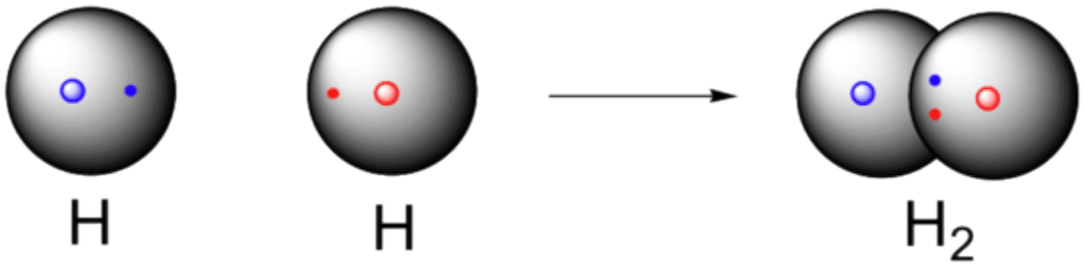
Introduction

As we have talked about using Lewis structures to depict the bonding in covalent compounds, we have been very vague in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

The **valence bond theory** is introduced to describe bonding in covalent molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. To explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

Example: The H_2 molecule

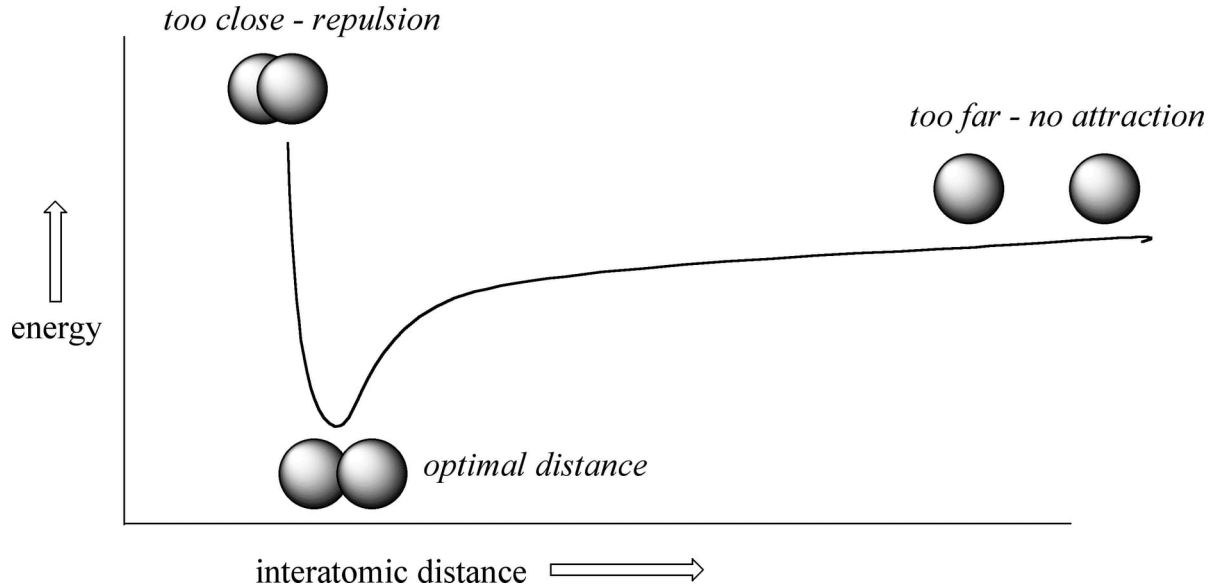
The simplest case to consider is the hydrogen molecule, H_2. When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1s orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals. In simple terms, we can say that both electrons now spend more time *between* the two nuclei and thus hold the atoms together. As we will see, the situation is not quite so simple as that, because the electron pair must still obey quantum mechanics - that is, the two electrons must now occupy a *shared orbital space*. This will be the essential principle of valence bond theory.



These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together.

How far apart are the two nuclei? That is a very important issue to consider. If they are too far apart, their respective 1s orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as

new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second. However, something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.



Graph of increasing energy against increasting interatomic distance. If the two are too close there is repulsion, if the two are too far there is no attraction. There is an optimal distance.

At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have a very unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**. For the H_2 molecule, this distance is 74 x 10^{-12} meters, or 0.74 Å (Å means angstrom, or 10^{-10} meters). Likewise, the difference in potential energy between the lowest state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond energy**. For the hydrogen molecule, this energy is equal to about 104 kcal/mol.

Every covalent bond in a given molecule has a characteristic length and strength. In general, carbon-carbon single bonds are about 1.5 Å long (Å means angstrom, or 10^{-10} meters) while carbon-carbon double bonds are about 1.3 Å, carbon-oxygen double bonds are about 1.2 Å, and carbon-hydrogen bonds are in the range of 1.0 – 1.1 Å. Most covalent bonds in organic molecules range in strength from just under 100 kcal/mole (for a carbon-hydrogen bond in ethane, for example) up to nearly 200 kcal/mole. You can refer to tables in reference books such as the CRC Handbook of Chemistry and Physics for extensive lists of bond lengths, strengths, and many other data for specific organic compounds.

Balls and Springs

Although we tend to talk about "bond length" as a specific distance, it is not accurate to picture covalent bonds as rigid sticks of unchanging length - rather, it is better to picture them as *springs* which have a defined length when relaxed, but which can be compressed, extended, and bent. This 'springy' picture of covalent bonds will become very important, when we study the analytical technique known as infrared (IR) spectroscopy.

Valence Bond Theory: A Localized Bonding Approach

You learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm (Figure 9.4.1). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a *maximum of two electrons with opposite spin*, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1s

atomic orbital of one hydrogen atom overlaps with the singly occupied 1s atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure 9.4.1).

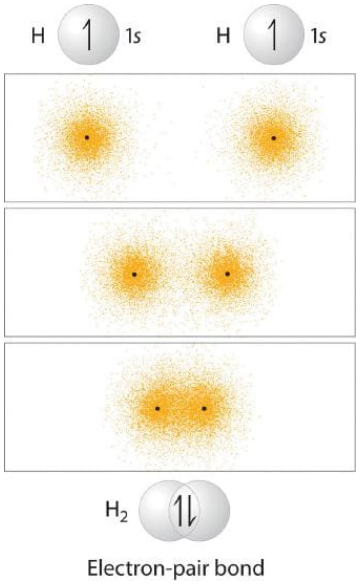


Figure 9.4.1: Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory, which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure 9.4.2 shows an electron-pair bond formed by the overlap of two *ns* atomic orbitals, two *np* atomic orbitals, and an *ns* and an *np* orbital where $n = 2$. Notice that bonding overlap occurs when the interacting atomic orbitals have the correct orientation (are "pointing at" each other) and are *in phase* (represented by colors in Figure 9.4.2).

> Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

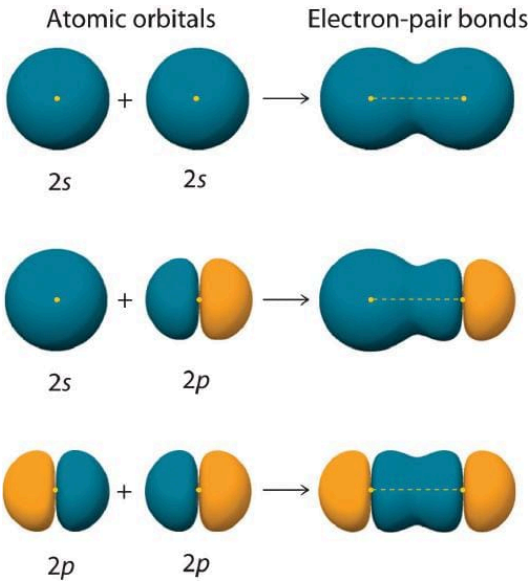


Figure 9.4.2 : Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two *ns* atomic orbitals (a), an *ns* and an *np* atomic orbital (b), and two *np* atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1s orbitals on the H atoms. If a singly occupied 1s orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion:



The ground state of beryllium has one electron pair in the 2s orbital. The excited state of beryllium takes one of the electrons from the 2s orbital and moves it to the 2p orbital.

In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1s orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2, the two Be–H bonds would not be equivalent: the 1s orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1s orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization.

Contributors and Attributions

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9.5: Hybrid Orbitals

The localized **valence bond theory** uses a process called **hybridization**, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

Hybridization of *s* and *p* Orbitals

In BeH_2, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure 9.5.1.

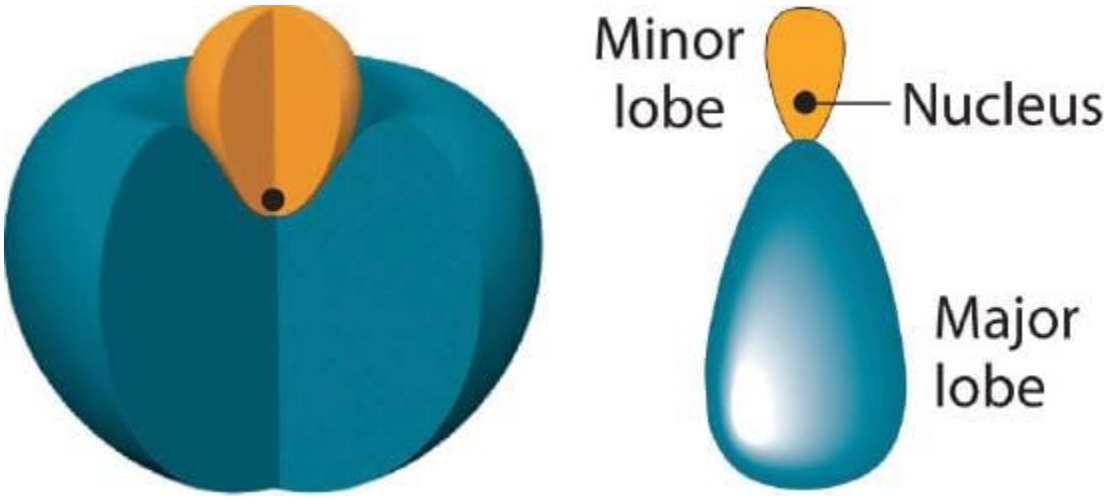


Figure 9.5.1**:** The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference A – B can also be written as A + (–B), in Figure 9.5.2 and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by –1 and adding. This gives us Equation 9.5.2, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{9.5.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{9.5.2}$$

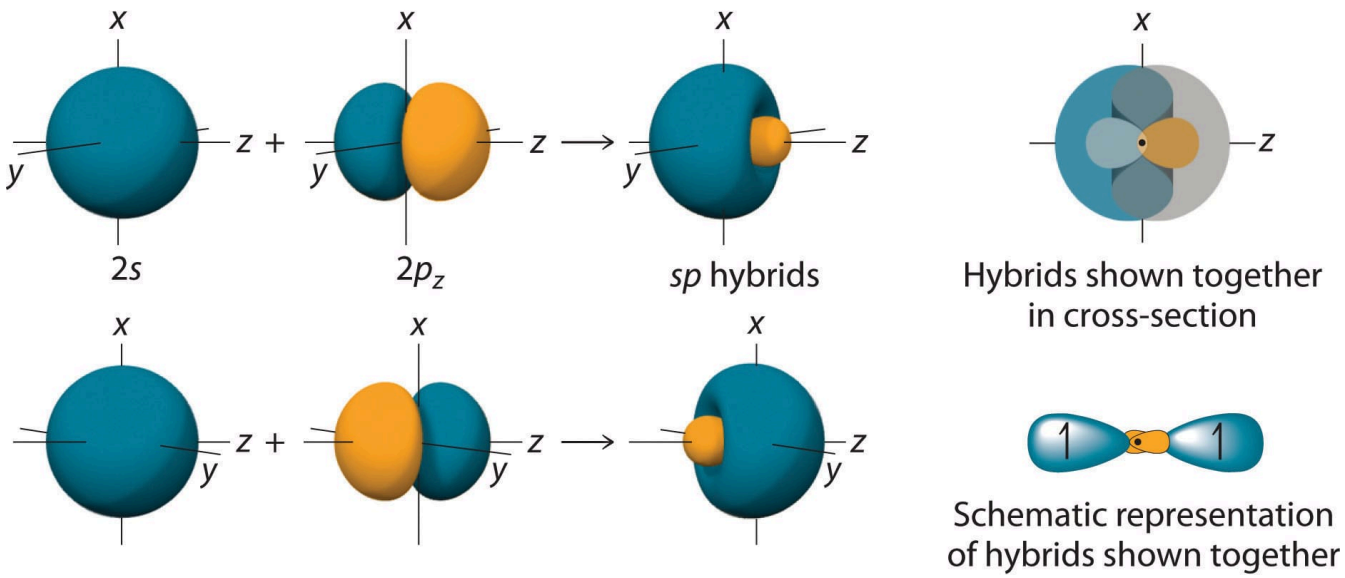


Figure 9.5.2: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one s and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure s and *p* orbitals, as illustrated in this diagram:

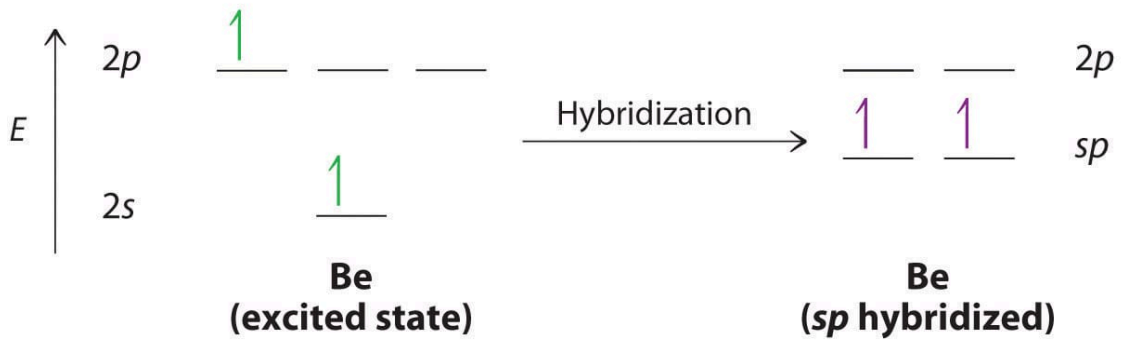


Figure 9.5.3. each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1s atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in BeH_2 are equivalent in energy and why BeH_2 has a linear geometry.

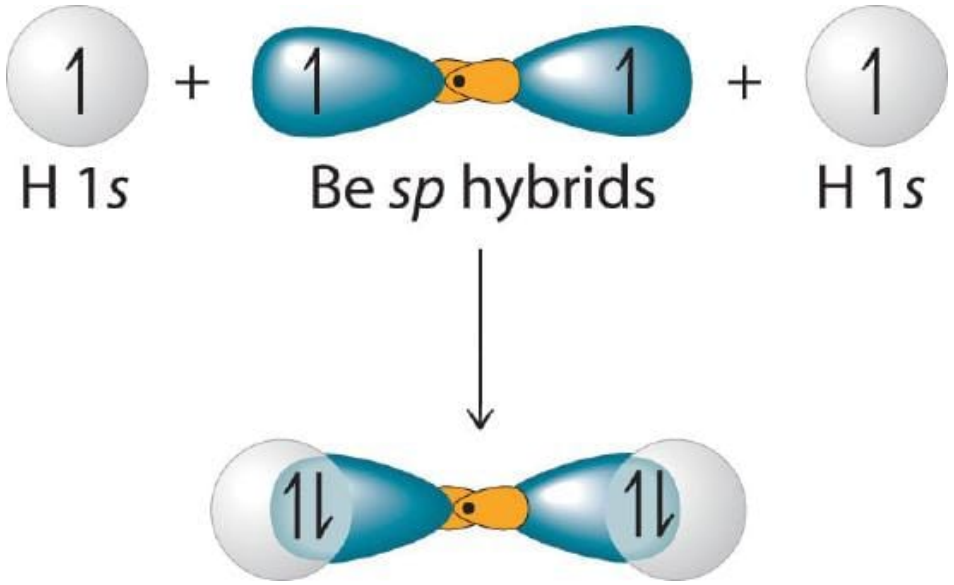


Figure 9.5.3: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1s orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule is linear.

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure 9.5.4). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

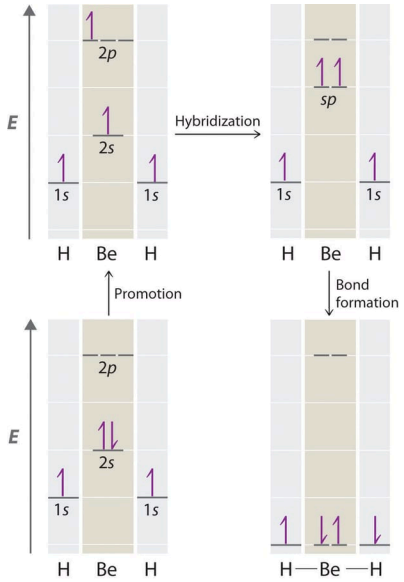


Figure 9.5.4: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable *only* if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.

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The concept of hybridization also explains why boron, with a $2s^2 2p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2*s* electrons to an unoccupied 2*p* orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2*s* and two 2*p* orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:

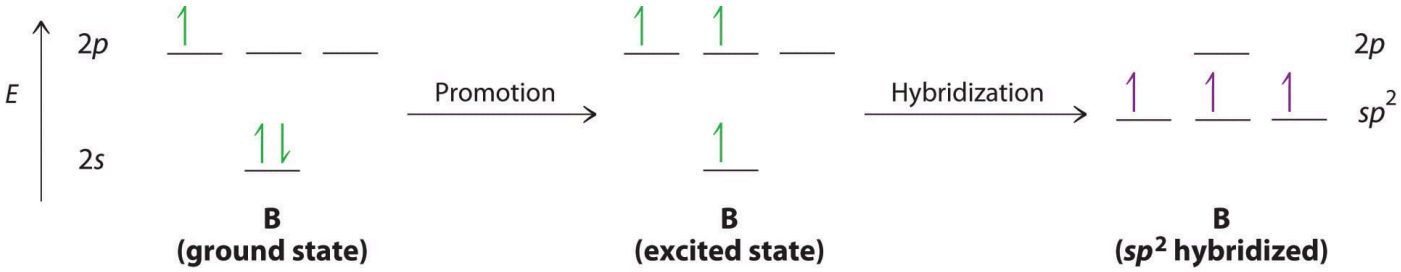


Figure 9.5.5). Because the hybrid atomic orbitals are formed from one s and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

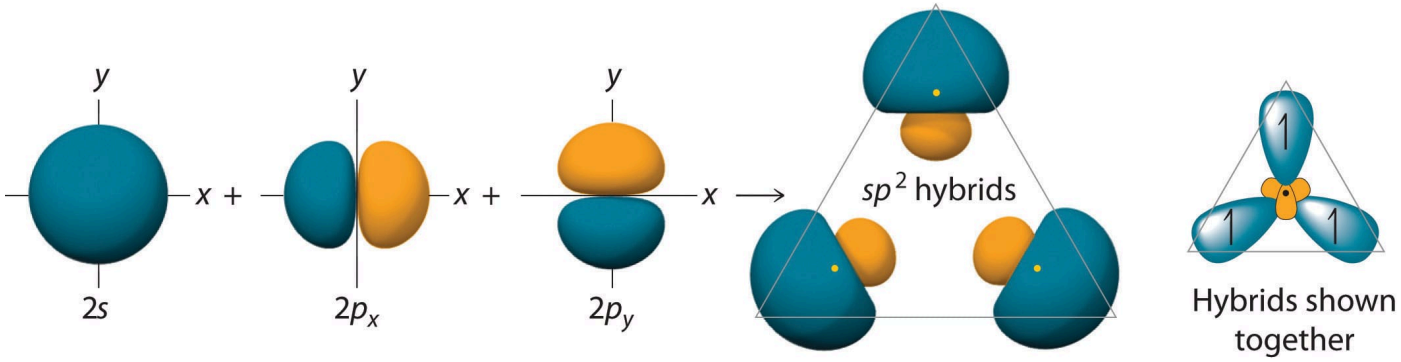


Figure 9.5.5: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

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Looking at the $2s^2 2p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give

a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:

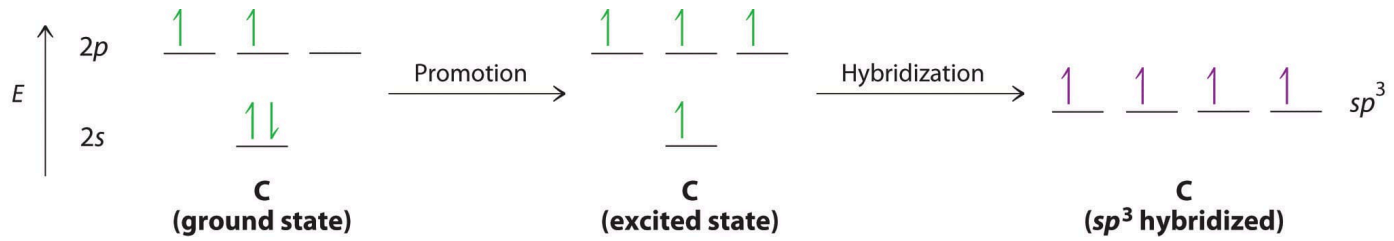


Figure 9.5.6). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy. Thus, methane (CH_4) is a tetrahedral molecule with four equivalent C-H bonds.

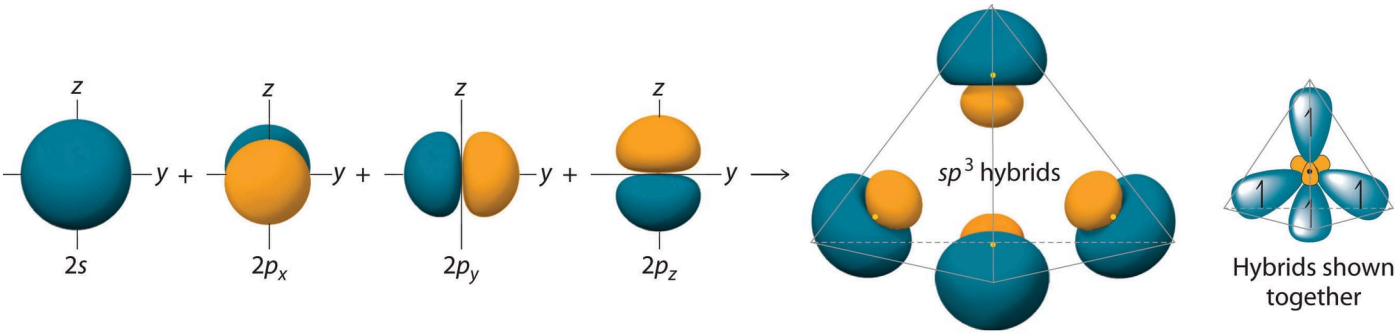


Figure 9.5.6: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that only form in certain chemical reactions.

Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.

The bonding in molecules such as NH_3 or H_2O, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3, for example, N, with a $2s^2 2p^3$ valence electron configuration, can hybridize its 2*s* and 2*p* orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:



The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O. Unfortunately, however, recent experimental evidence indicates that in NH_3 and H_2O, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

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Example 9.5.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A. Using the VSEPR approach to determine the number of electron pairs and the molecular geometry of the molecule.
B. From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

1. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^2 3p^4$ valence electron configuration with six electrons, but by hybridizing its 3*s* and 3*p* orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^2 2p^2$ valence electron configuration. By hybridizing its 2*s* and 2*p* orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise 9.5.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion
b. hydrazine ($H_2N–NH_2$)

Answer a available at the end of this section.

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

Hybridization Using d Orbitals

Hybridization is not restricted to the *ns* and *np* atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence $(n - 1)d$ orbitals as well as its *ns* and *np* orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in PF_5 and SF_6). Using the *ns* orbital, all three *np* orbitals, and one $(n - 1)d$ orbital gives a set of five sp^3d hybrid orbitals that point toward the vertices of a trigonal bipyramid (part (a) in Figure 9.5.7). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the *ns* orbital, all three *np* orbitals, and *two nd* orbitals gives a set of six equivalent sp^3d^2 hybrid orbitals oriented toward the vertices of an octahedron (part (b) in Figure 9.5.6). In the VSEPR model, PF_5 and SF_6 are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which sp^3d or sp^3d^2 hybrid orbitals are used for bonding.

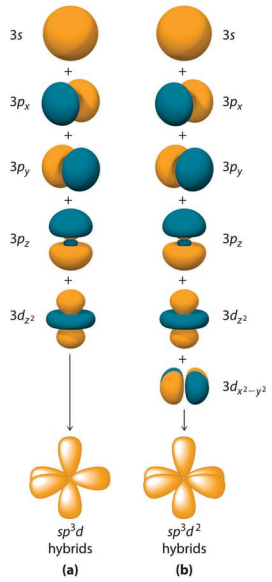


Figure 9.5.7: Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

Example 9.5.2

What is the hybridization of the central atom in each species? Describe the bonding in each species.

a. XeF_4
b. SO_4^{2-}
c. SF_4

Given: three chemical species

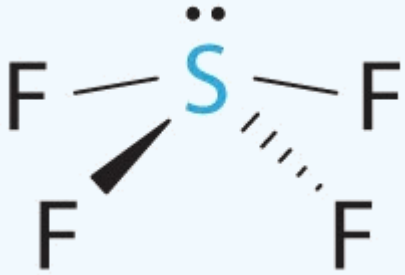
Asked for: hybridization of the central atom

Strategy:

A. Determine the geometry of the molecule using the strategy in Example 9.5.1. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.
B. Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

Solution:

a. **A** Using the VSEPR model, we find that Xe in XeF_4 forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be sp^3d^2 hybridized. **B** With 12 electrons around Xe, four of the six sp^3d^2 hybrid orbitals form Xe–F bonds, and two are occupied by lone pairs of electrons.
b. **A** The S in the SO_4^{2-} ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be sp^3 hybridized to generate four S–O bonds. **B** Filling the sp^3 hybrid orbitals with eight electrons from four bonds produces four filled sp^3 hybrid orbitals.
c. **A** The S atom in SF_4 contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:



To accommodate five electron pairs, the sulfur atom must be sp^3d hybridized. **B** Filling these orbitals with 10 electrons gives four sp^3d hybrid orbitals forming S–F bonds and one with a lone pair of electrons.

Exercise 9.5.2

What is the hybridization of the central atom in each species? Describe the bonding.

a. PCl_4^+
b. BrF_3
c. SiF_6^{2-}

Answer a available at the end of this section.

Hybridization using *d* orbitals allows chemists to explain the structures and properties of many molecules and ions. Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).

Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides (CF_4 and SiF_4), only SiF_4 reacts with F^- to give a stable hexafluoro dianion, SiF_6^{2-}. Because there are no 2*d* atomic orbitals, the formation of octahedral CF_6^{2-} would require hybrid orbitals created from 2*s*, 2*p*, and 3*d* atomic orbitals. The 3*d* orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp^3d^2 hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF_6^{2-} have never been prepared.

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Example 9.5.3: OF_4

What is the hybridization of the oxygen atom in OF_4? Is OF_4 likely to exist?

Given: chemical compound

Asked for: hybridization and stability

Strategy:

A. Predict the geometry of OF_4 using the VSEPR model.
B. From the number of electron pairs around O in OF_4, predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

Solution:

A The VSEPR model predicts that OF_4 will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. **B** To accommodate five electron pairs, the O atom would have to be sp^3d hybridized. The only *d* orbital available for forming a set of sp^3d hybrid orbitals is a 3*d* orbital, which is *much* higher in energy than the 2*s* and 2*p* valence orbitals of oxygen. As a result, the OF_4 molecule is unlikely to exist. In fact, it has not been detected.

Exercise 9.5.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer a available at the end of this section.

Summary

Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach. The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled ns^2 subshell to an empty *np* or $(n - 1)d$ valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an *ns* and an *np* orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of an *ns* and two or three *np* orbitals produces three equivalent sp^2 **hybrids** or four equivalent sp^3 **hybrids**, respectively. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two $(n - 1)d$ orbitals to give sets of five sp^3d or six sp^3d^2 **hybrid** orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

Answers

Exercise 9.5.1

B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.

Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

Exercise 9.5.2

sp^3 with four P–Cl bonds

sp^3d with three Br–F bonds and two lone pairs

sp^3d^2 with six Si–F bonds

Exercise 9.5.3

sp^3d^2 hybridization; no

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9.6: Multiple Bonds

Learning Objectives

- To explain resonance structures using molecular orbitals.

So far in our valence bond orbital descriptions we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using **molecular orbitals** formed by unhybridized *np* atomic orbitals.

Multiple Bonding

We begin our discussion by considering the bonding in ethylene (C_2H_4). Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied s orbital on each H and a singly occupied sp^2 lobe on the other C. The sp^2 hybridization can be represented as follows:

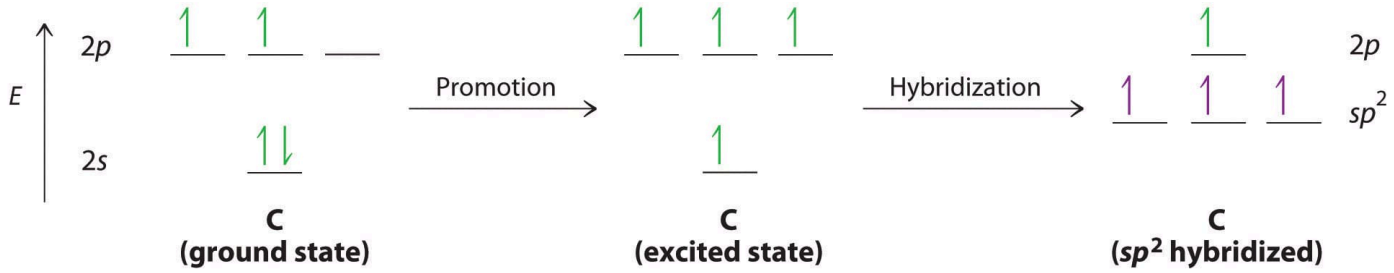


Figure 9.6.1). These two singly occupied $2p_z$ orbitals can overlap in a side-to-side fashion to form a π bond. The orbitals overlap both above and below the plane of the molecule but form just one bonding orbital space. The C–C π bond plus the hybridized C–C σ bond together form a double bond.

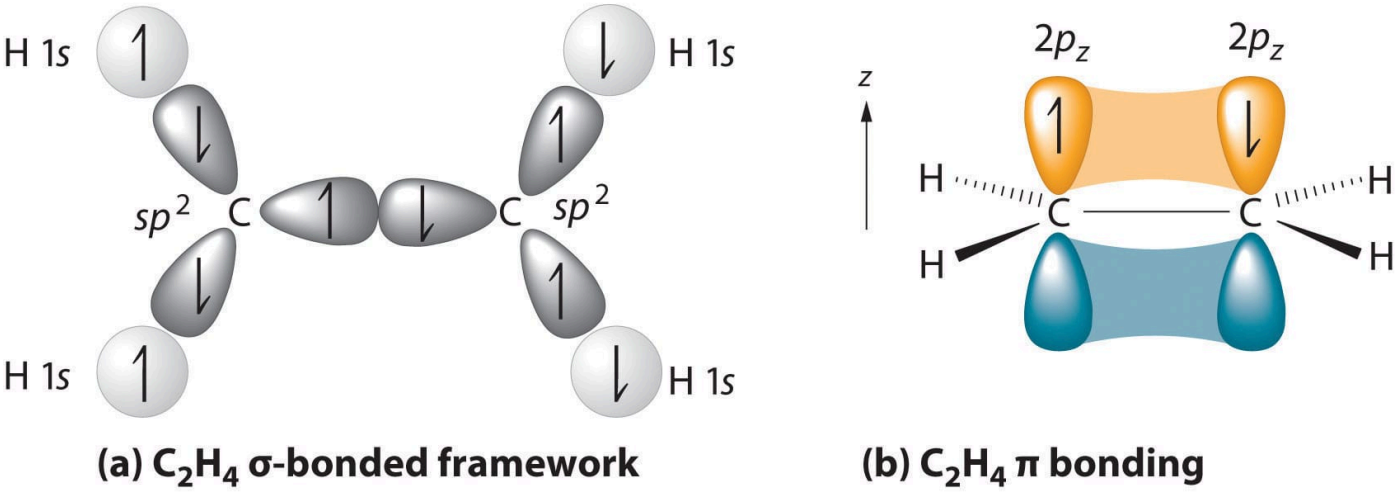
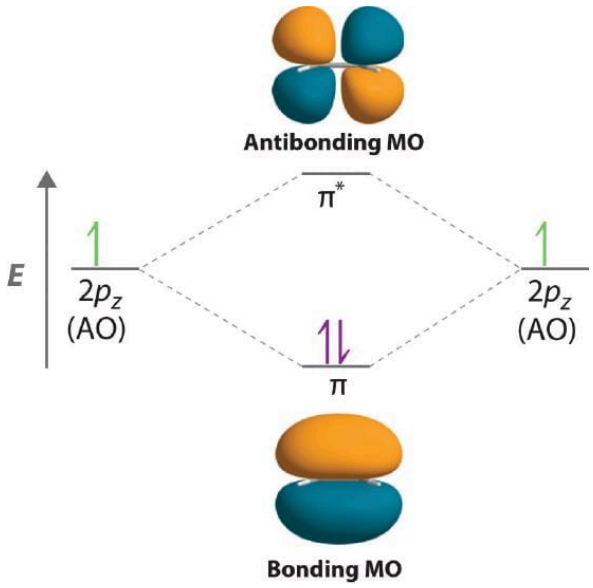


Figure 9.6.1: Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.)

When considering multiple bonds, we can introduce the more sophisticated **molecular orbital theory** to better understand how orbital overlap creates bonding orbitals. Recall that atomic orbitals represent *electron wavefunctions*; this implies that

"orbital overlap" actually involves the combination of those wavefunctions, which can occur via both constructive and destructive interference. Thus, when the two singly occupied $2p_z$ orbitals in ethylene overlap, they actually create both a π bonding orbital (constructive combination) and a π^* antibonding orbital (destructive combination), which produces the energy-level diagram shown in Figure 9.6.2. With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. Electrons occupying this orbital lower the potential energy of the combination and tend to hold the two nuclei together (i.e., they form a bond.) The π^* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis; electrons in this orbital would tend to push the nuclei apart, so it is called an antibonding orbital. Because each $2p_z$ orbital has a single electron, there are only two electrons, enough to fill only the bonding (π) level, leaving the π^* orbital empty. Consequently, the C–C bond in ethylene consists of a σ bond and a π bond, which together give a C=C double bond. Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two CH_2 fragments are coplanar, which maximizes the overlap of the two singly occupied $2p_z$ orbitals.



IFigure 9.6.2: Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene. As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.

Triple bonds, as in acetylene (C_2H_2), can also be explained using a combination of hybrid atomic orbitals and molecular orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is *sp* hybridized. If one *sp* lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized 2*p* orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure 9.6.3).

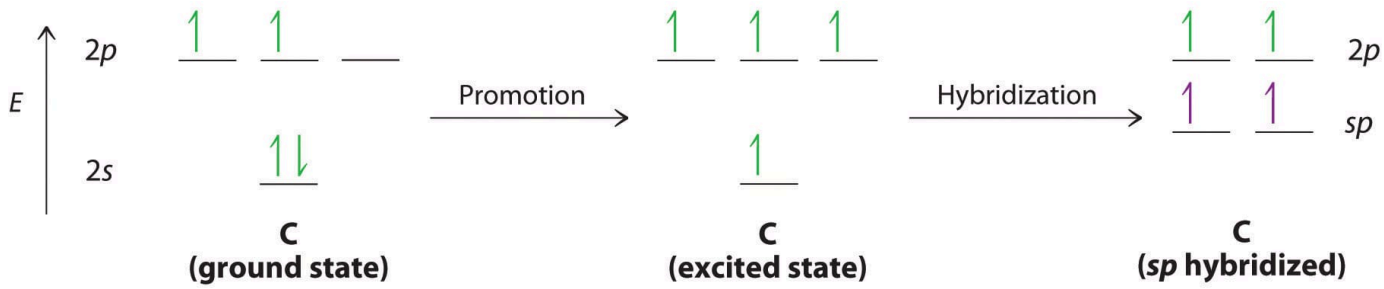


Figure 9.6.2). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.

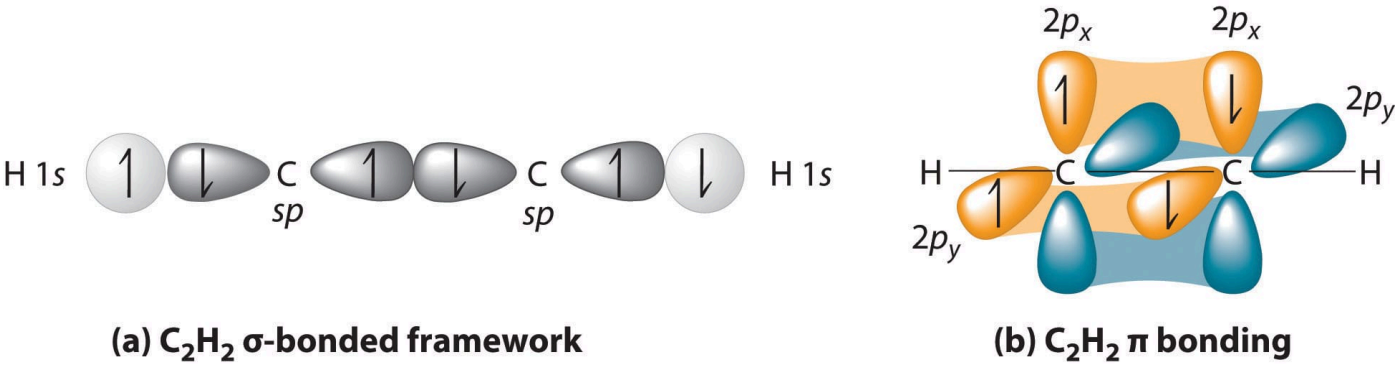


Figure 9.6.3: Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon *sp* hybrid orbitals and two singly occupied hydrogen 1s orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.

In complex molecules, *hybrid orbitals* and *valence bond theory* can be used to describe σ bonding, and unhybridized π orbitals and *molecular orbital theory* can be used to describe π bonding.

Example 9.6.1

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

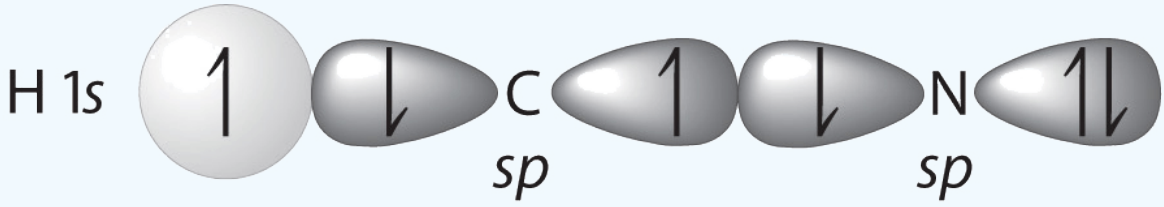
Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

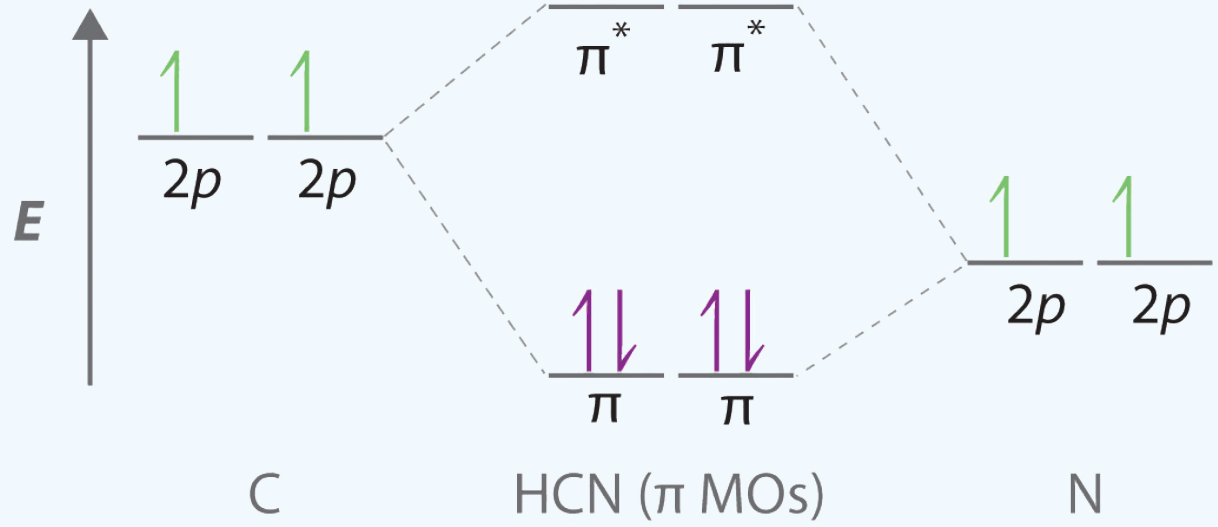
A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.
B. Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals to form π and π^* orbitals.
C. Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.

Solution:

A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of *sp* hybridization at carbon. Because the nitrogen atom can also be described as *sp* hybridized, we can use one *sp* hybrid on each atom to form a C–N σ bond. This leaves one *sp* hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:



B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized 2*p* atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four 2*p* atomic orbitals can be combined to give four molecular orbitals: two π (bonding) orbitals and two π^* (antibonding) orbitals. **C** With 4 electrons available, only the π orbitals are filled. The overall result is a triple bond (1 σ and 2 π) between C and N.



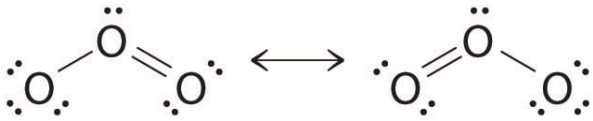
Exercise 9.6.1

Describe the bonding in formaldehyde ($H_2C{=}O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer available at the end of this section.

Molecular Orbitals and Resonance Structures

Resonance structures can be used to describe the bonding in molecules such as ozone (O_3) and the nitrite ion (NO_2^-). Ozone can be represented by either of these Lewis electron structures:



Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

Experimental evidence indicates that ozone has a bond angle of 117.5°. Because this angle is close to 120°, it is likely that the central oxygen atom in ozone is trigonal planar and sp^2 hybridized. If we assume that the terminal oxygen atoms are also sp^2 hybridized, then we obtain the σ-bonded framework shown in Figure 9.6.4. Two of the three sp^2 lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that are also in sp^2 lobes. In addition, each oxygen atom has one unhybridized 2*p* orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so O_3 has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized 2*p* orbitals.

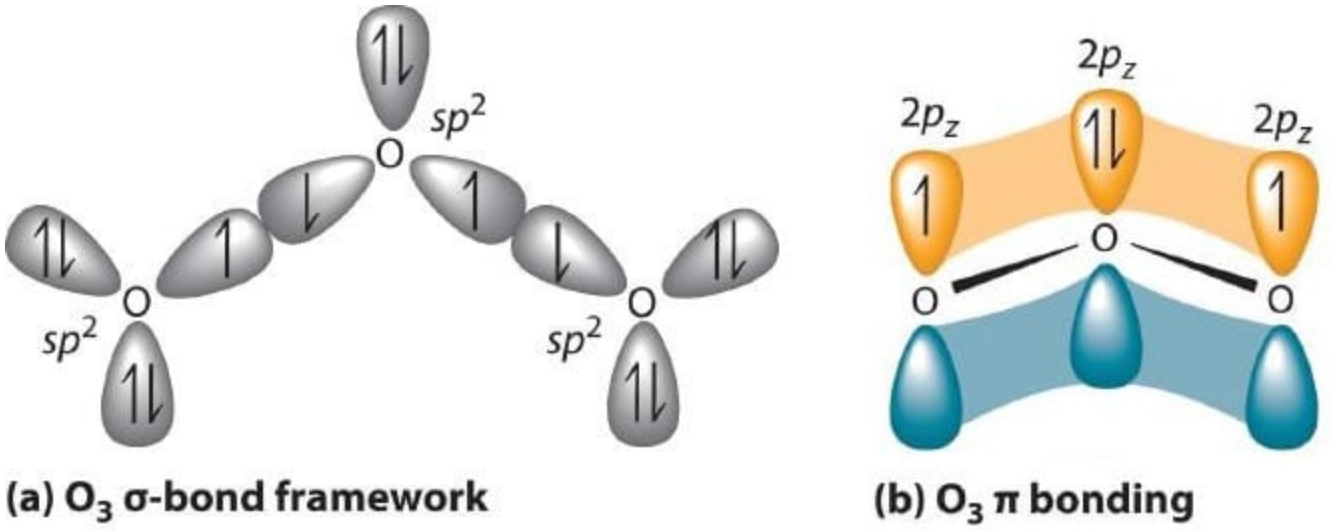


Figure 9.6.4: Bonding in Ozone. (a) In the formation of the σ-bonded framework, three sets of oxygen sp^2 hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O_3. (b) One unhybridized $2p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized $2p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized $2p_z$ orbital on the central O atom has 2 electrons.

With a molecular orbital approach to describe the π bonding, three 2*p* atomic orbitals give us three molecular orbitals, as shown in Figure 9.6.5. One of the molecular orbitals is a π bonding molecular orbital, which is shown as a banana-shaped region of electron density above and below the molecular plane. This region has *no* nodes perpendicular to the O_3 plane. The molecular orbital with the highest energy has two nodes that bisect the O–O σ bonds; it is a π^* antibonding orbital. The third molecular orbital contains a single node that is perpendicular to the O_3 plane and passes through the central O atom; because the orbital nodes do not directly touch, this is a *nonbonding* molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

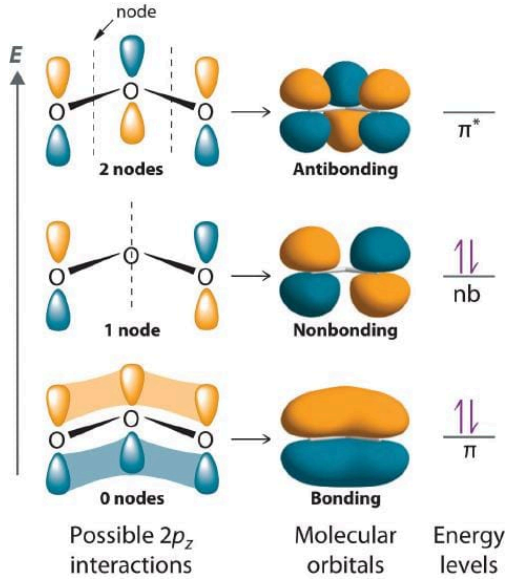


Figure 9.6.5: π Bonding in Ozone. The three unhybridized $2p_z$ atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π^* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this diagram fills the bonding and nonbonding orbitals. With one filled π bonding orbital holding three atoms together, the net π bond order is ½ per O–O bond. The combined σ/π bond order is thus 1 ½) for each O–O bond.

We can now place the remaining four electrons in the three energy levels shown in Figure 9.6.5, thereby filling the π bonding and the nonbonding levels. The result is a single π bond holding three oxygen atoms together, or ½π bond per O–O. We therefore predict the overall O–O bond order to be ½π bond plus 1 σ bond), just as predicted using resonance structures. The molecular

orbital description, however, makes it more clear that resonance really means that electrons are *delocalized* over all three atoms at once. The molecular orbital approach also shows that the π nonbonding orbital is localized on the terminal O atoms, which suggests that they are more electron rich than the central O atom (corresponding to the "extra" lone pair seen on one of the terminal O atoms in the Lewis resonance structures). The reactivity of ozone is consistent with the predicted charge localization.

Resonance structures are a crude way of describing molecular orbitals that extend over more than two atoms.

Example 9.6.2

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and molecular orbitals. Lewis dot structures and the VSEPR model predict that the NO_2^- ion is bent.

Given: chemical species and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

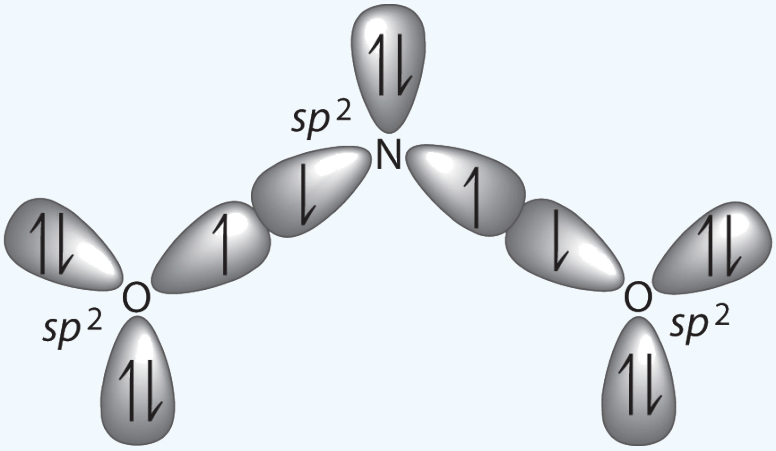
Strategy:

A. Calculate the number of valence electrons in NO_2^-. From the structure, predict the type of atomic orbital hybridization in the ion.
B. Predict the number and type of molecular orbitals that form during bonding. Use valence electrons to fill these orbitals and then calculate the number of electrons that remain.
C. If there are unhybridized orbitals, place the remaining electrons in these orbitals in order of increasing energy. Calculate the bond order and describe the bonding.

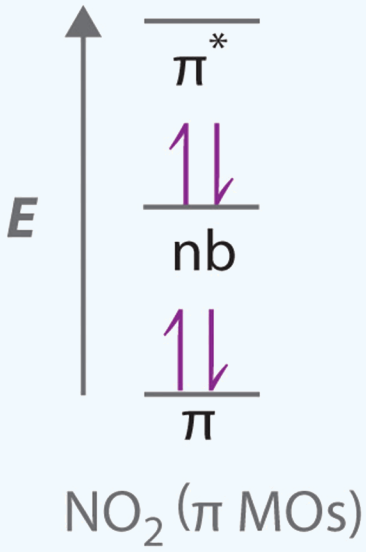
Solution:

A The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in NO_2^- is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the –1 charge). The bent structure implies that the nitrogen is sp^2 hybridized.

B If we assume that the oxygen atoms are sp^2 hybridized as well, then we can use two sp^2 hybrid orbitals on each oxygen and one sp^2 hybrid orbital on nitrogen to accommodate the five lone pairs of electrons. Two sp^2 hybrid orbitals on nitrogen form σ bonds with the remaining sp^2 hybrid orbital on each oxygen. The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized 2*p* orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these three 2*p* orbitals interact to form bonding, nonbonding, and antibonding π molecular orbitals. The bonding molecular orbital is spread over the nitrogen and both oxygen atoms.



C Placing 4 electrons in the energy-level diagram fills both the bonding and nonbonding molecular orbitals and gives a π bond order of 1/2 per N–O bond. The overall N–O bond order is $1\ \frac{1}{2}$, consistent with a resonance structure.



Exercise 9.6.2

Describe the bonding in the formate ion (HCO_2^-), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

Answer available at the end of this section.

The Chemistry of Vision

Hydrocarbons in which two or more carbon–carbon double bonds are directly linked by carbon–carbon single bonds (called *conjugated* structures) are generally more stable than expected because of resonance. Because the double bonds are close enough to interact electronically with one another, the π electrons are shared over all the carbon atoms, as illustrated for 1,3-butadiene in Figure 9.6.6. As the number of interacting atomic orbitals increases, the number of molecular orbitals increases, the energy spacing between molecular orbitals decreases, and the systems become more stable (Figure 9.6.7). Thus as a chain of alternating double and single bonds becomes longer, the energy required to excite an electron from the highest-energy occupied (bonding) orbital to the lowest-energy unoccupied (antibonding) orbital decreases. If the chain is long enough, the amount of energy required to excite an electron corresponds to the energy of visible light. For example, vitamin A is yellow because its chain of five alternating double bonds is able to absorb violet light. Many of the colors we associate with dyes result from this same phenomenon; most dyes are organic compounds with alternating double bonds.

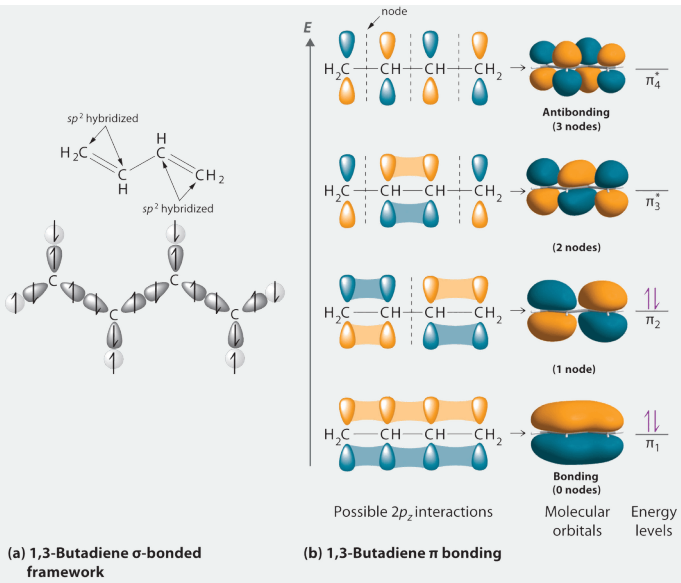


Figure 9.6.6: π Bonding in 1,3-Butadiene. (a) If each carbon atom is assumed to be sp^2 hybridized, we can construct a σ-bonded framework that accounts for the C–H and C–C single bonds, leaving *four* singly occupied $2p_z$ orbitals, one on each carbon atom. (b) As in ozone, these orbitals can interact, in this case to form *four* molecular orbitals. The molecular orbital at lowest energy is a bonding orbital with 0 nodes, the one at highest energy is antibonding with 3 nodes, and the two in the middle have 1 node and 2 nodes and are somewhere between bonding or antibonding and nonbonding, respectively. The energy of the molecular orbital increases with the number of nodes. With four electrons, only the two bonding orbitals are filled, consistent with the presence of two π bonds.

As the number of atomic orbitals increases, the difference in energy between the resulting molecular orbital energy levels decreases, which allows light of lower energy to be absorbed. As a result, organic compounds with long chains of carbon atoms and alternating single and double bonds tend to become more deeply colored as the number of double bonds increases.

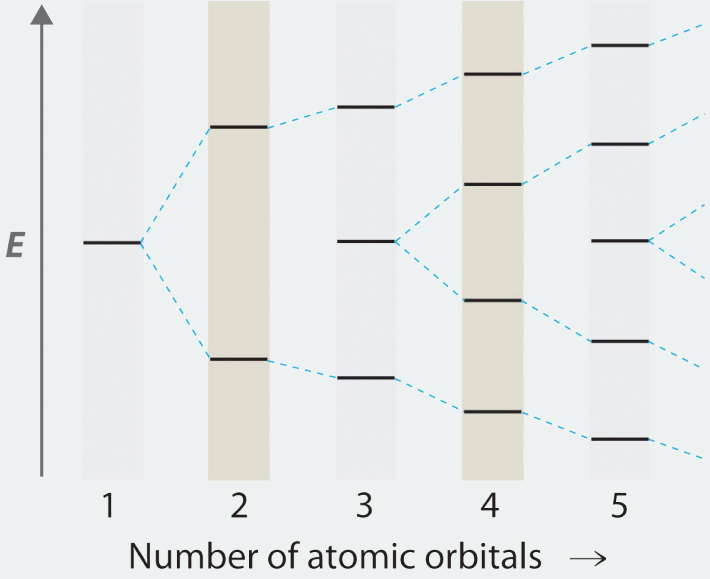


Figure 9.6.7: Molecular Orbital Energy-Level Diagrams for a Chain of *n* Like Orbitals That Interact ($n \leq 5$).

As the number of interacting atomic orbitals increases, the energy separation between the resulting molecular orbitals steadily decreases.

A derivative of vitamin A called *retinal* is used by the human eye to detect light and has a structure with alternating C=C double bonds. When visible light strikes retinal, the energy separation between the molecular orbitals is sufficiently close that the energy absorbed corresponds to the energy required to change one double bond in the molecule from *cis*, where like groups are on the same side of the double bond, to *trans*, where they are on opposite sides, initiating a process that causes a signal to be sent to the brain. If this mechanism is defective, we lose our vision in dim light. Once again, a molecular orbital approach to bonding explains a process that cannot be explained using any of the other approaches we have described.

Summary

Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding. To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized *np* orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as O_2 and N_2. Applying the same approach to π bonding between three or four atoms requires combining three or four unhybridized *np* orbitals on adjacent atoms to generate π bonding, antibonding, and nonbonding molecular orbitals extending over all of the atoms. Filling the resulting energy-level diagram with the appropriate number of electrons explains the bonding in molecules or ions that previously required the use of resonance structures in the Lewis electron-pair approach.

Answers

Exercise $9.6.1$

- σ-bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C–H bonds, and one sp^2 hybrid orbital on C and O forms a C–O σ bond.
- π bonding: Unhybridized, singly occupied 2*p* atomic orbitals on carbon and oxygen interact to form π (bonding) and π^* (antibonding) molecular orbitals. With two electrons, only the π (bonding) orbital is occupied.

Exercise$9.6.2$

Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of sp^2 hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized 2*p* orbitals (on C and both O atoms) form three π molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding π molecular orbitals. The overall C–O bond order is therefore $frac32$

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9.7: Molecular Orbitals

Learning Objectives

- To use molecular orbital theory to predict bond order

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a *delocalized* approach to bonding.

Molecular Orbital Theory: A Delocalized Bonding Approach

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As we explained in Chapter 9, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The 1s atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1s wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) = &\quad AO(atom\ A) &+ &\quad AO(atom B) \\ MO(1) = &\quad AO(atom\ A) &- &\quad AO(atom B) \end{aligned} \tag{9.7.1}$$

The molecular orbitals created from Equation 9.7.1 are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.

> A molecule must have as many molecular orbitals as there are atomic orbitals.

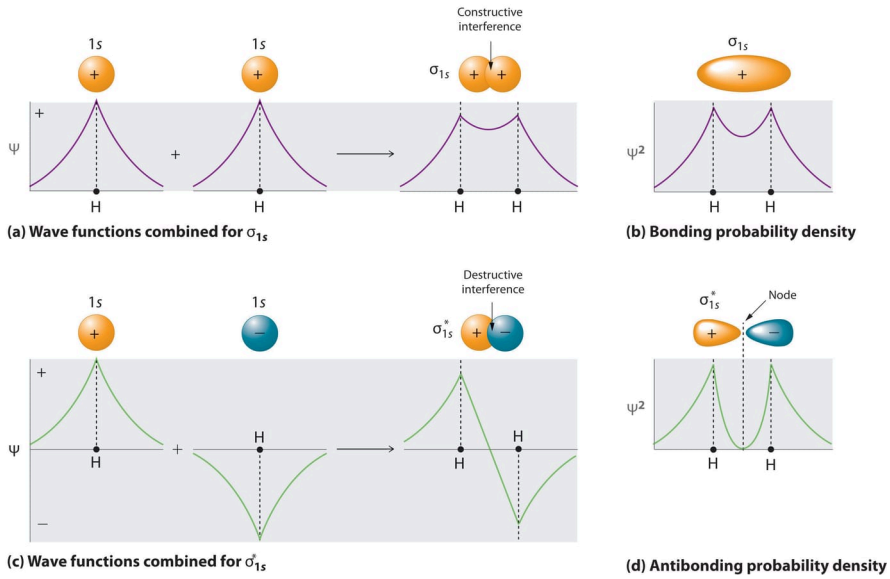


Figure 9.7.1: Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the *square* of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1s orbitals is called a σ_{1s} combination (pronounced "sigma one ess") (part (a) and part (b) in Figure 9.7.1). In a sigma (σ) orbital, (i.e., a bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry), the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1s denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{9.7.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 9.7.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} ("sigma one ess star"). In a sigma star (σ^*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^\star_{1s} \approx 1s\,(A) - 1s\,(B) \tag{9.7.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the $\sigma^\star_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^\star_{1s}$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1s atomic orbitals. Conversely, electrons in the $\sigma^{\star}_{1s}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1s atomic orbitals. Consequently, the $\sigma^{\star}_{1s}$ molecular orbital has a *higher* energy than either of the hydrogen 1s atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1s atomic orbitals, and the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure $9.7.2$

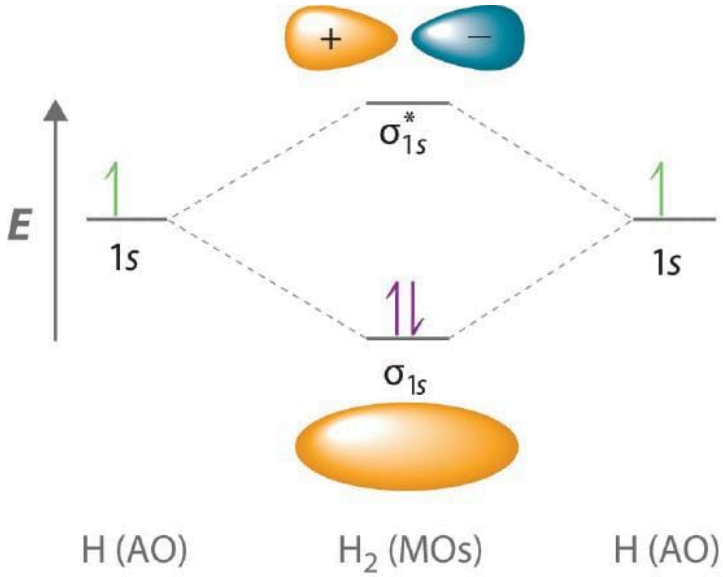


Figure $9.7.2$: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1s atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> A bonding molecular orbital is *always* lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is *always* higher in energy (less stable).

To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure $9.7.2$). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$bond\ order = \frac{number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons}{2} \tag{9.7.4}$$

To calculate the bond order of H_2, we see from Figure $9.7.2$ that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2}=1 \tag{9.7.5}$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3. We can use energy-level diagrams such as the one in Figure 9.7.2 to describe the bonding in other pairs of atoms and ions where *n* = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

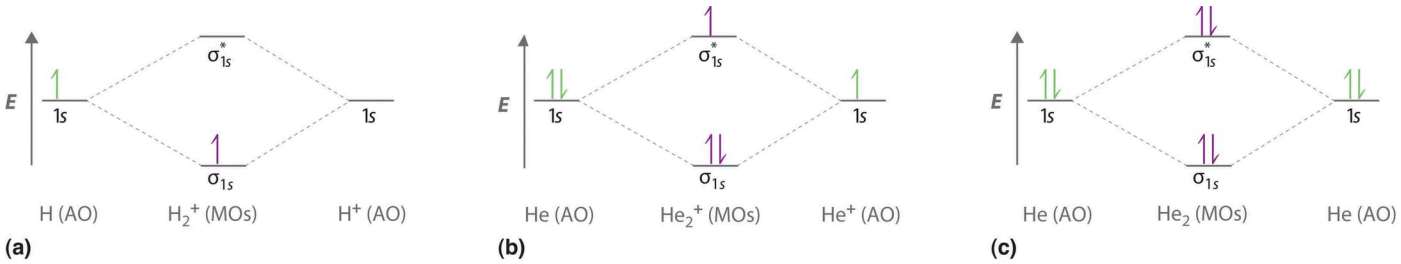


Figure 9.7.3: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

for the H2+ ion the H has one unpaired electron in the 1s orbital so the H2+ has one unpaired electron in the sigmas 1 s orbital. for He2+ ion, He has a full 1 s orbital and He+ has one upaired electron in the 1 s orbital. This means that the sigmal 1s orbital is full and the sigmal*1s orbital has one upaired electron. For the He2 molecule, each He has a full 1 s orbital. This means that sigma 1s and sigma * 1s orbital are full.

Figure 9.7.3*a* shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is

$$\frac{1-0}{2}=1/2$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 9.7.1, these predictions agree with the experimental data.

Figure 9.7.3*b* is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma^\star_{1s}$ antibonding orbital, giving a $(\sigma_{1s})^2(\sigma^\star_{1s})^1$ electron configuration. This electron configuration gives a bond order of

$$\frac{2-1}{2}=1/2$$

As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 9.7.1).

Table 9.7.1: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma^\star_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^\star_{1s})^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure $9.7.3c$ is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ^*_{1s} antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2 (\sigma^*_{1s})^2$ electron configuration, with a predicted bond order of (2 – 2) ÷ 2 = 0, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

> In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

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Example 9.7.1

Use a molecular orbital energy-level diagram, such as those in Figure $9.7.2$, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

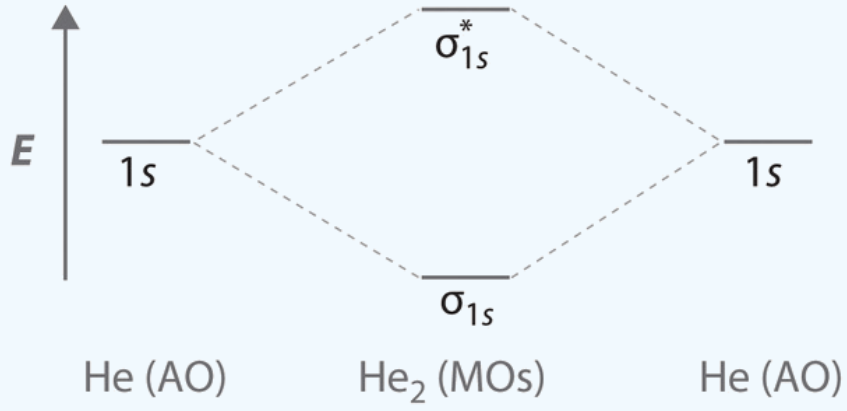
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

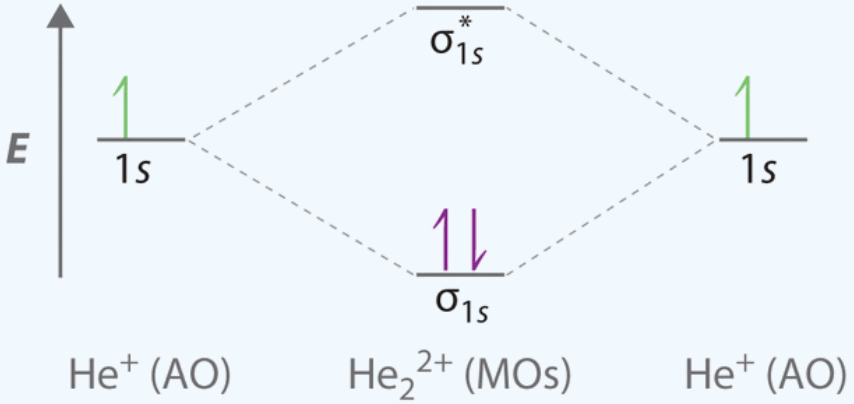
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbital
B. s. Draw the molecular orbital energy-level diagram for the system.
C. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
D. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1s atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ^*_{1s} antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1s atomic orbital. We can now fill the molecular orbital diagram:



Each He+ has one unpaired electron in the 1 s orbital. This means that He2 2+ has a full sigma 1 s orbital.

The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise 9.7.1

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer available at the end of this section.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from

valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 9.7.4, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in Figure 9.7.4. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

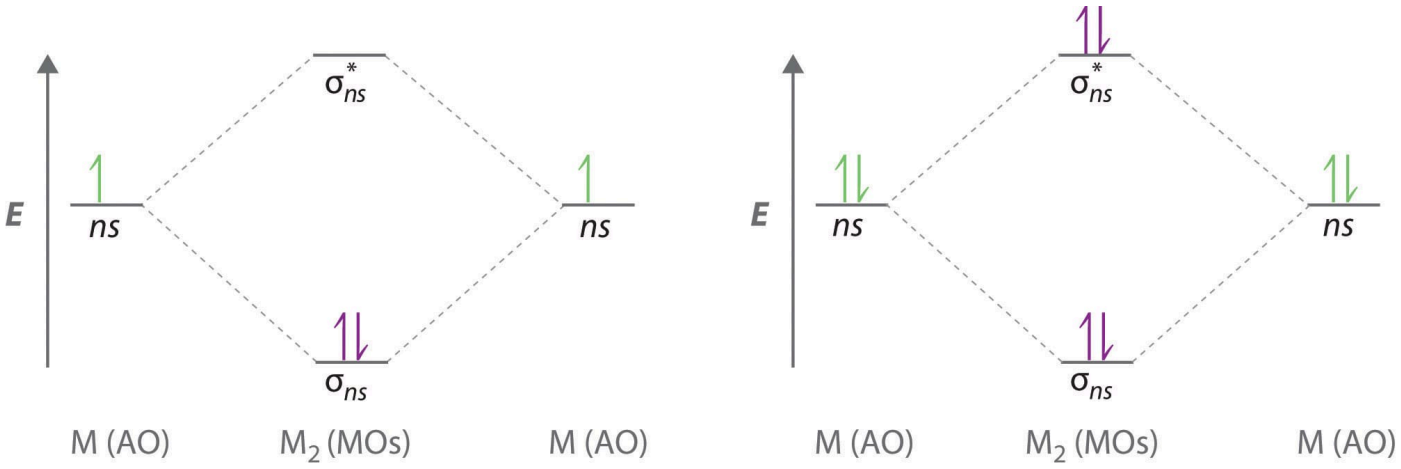


Figure 9.7.4 : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns}* (nonbonding) levels, leading to a predicted bond order of 0.

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure 9.7.2 . As shown in part (b) in Figure 9.7.4, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

Example 9.7.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

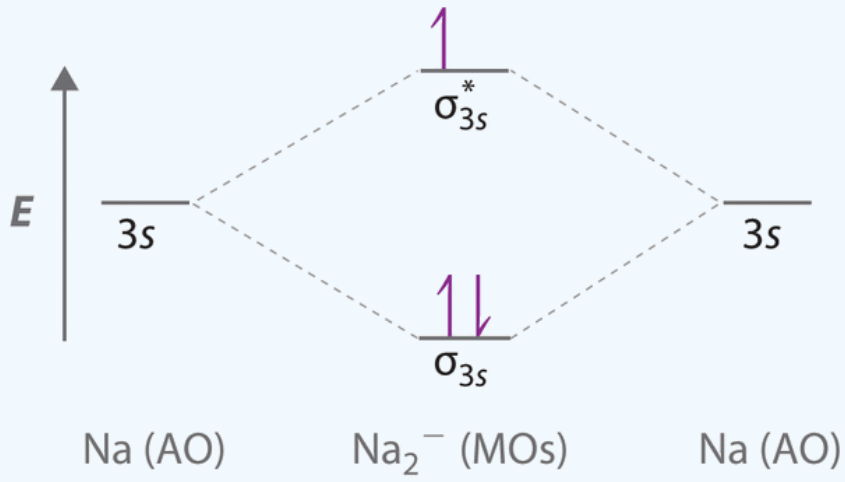
Strategy:

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.

B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1s atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s^*} and a $(\sigma_{3s})^2 (\sigma_{3s}^*)^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise 9.7.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer available at the end of this section.

Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{9.7.6}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 9.7.5, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{9.7.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z\,(A) + np_z\,(B) \tag{9.7.8}$$

In this combination, shown in part (b) in Figure $9.7.5$, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z\,(A) - np_z\,(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

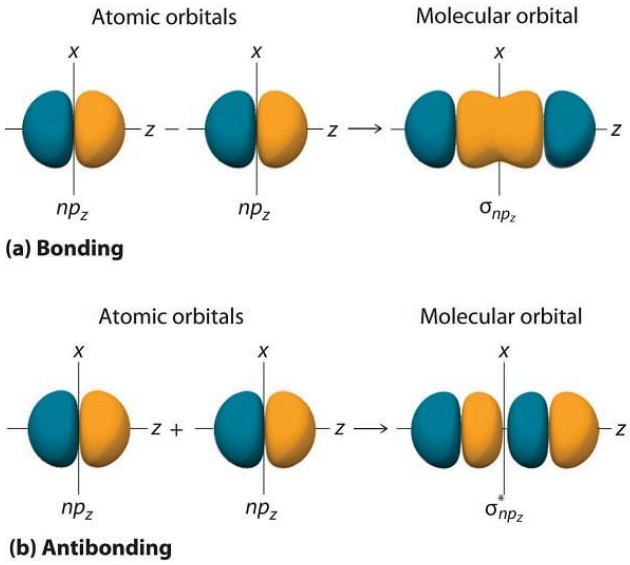


Figure $9.7.5$ Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate – + – +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

> Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure $9.7.6$, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{9.7.9}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{9.7.10}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y}molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

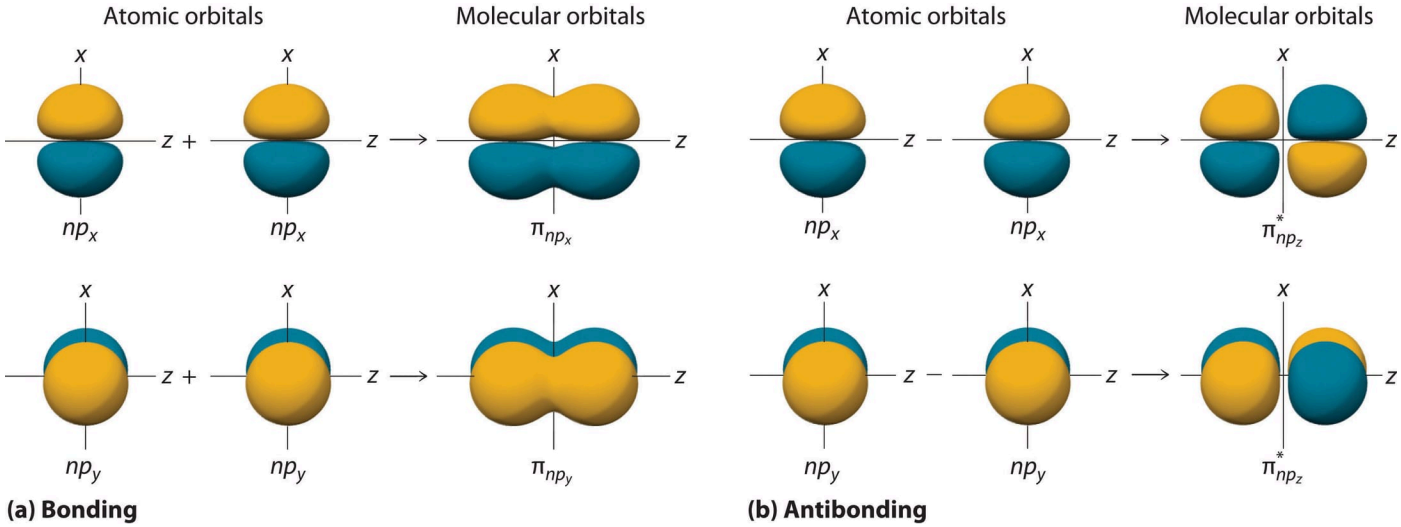


Figure 9.7.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure 9.7.7 is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

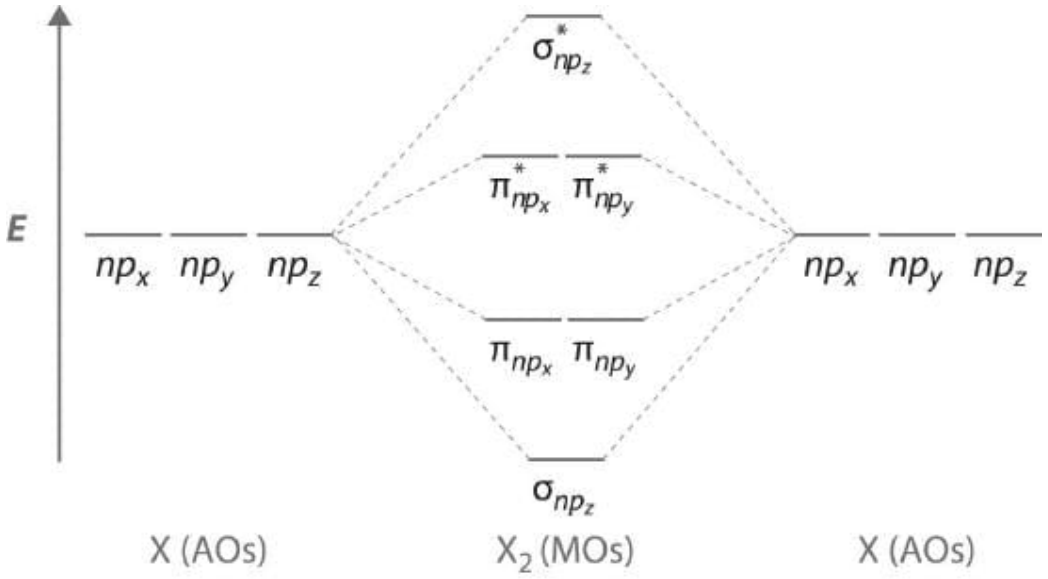


Figure 9.7.7 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic

orbital on one atom with an np_z atomic orbital on another. As shown in Figure 9.7.8, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

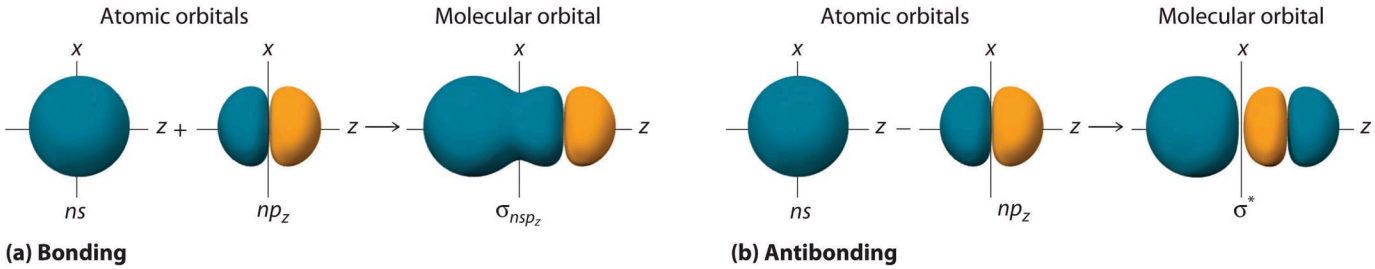


Figure 9.7.8 : Formation of Molecular Orbitals from an *ns* Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Summary

Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach. A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic

orbitals.

Answers

Exercise 9.7.1

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2 (\sigma^\star_{1s})^2$ with a bond order of 0. It is therefore predicted to be unstable.

Exercise 9.7.2

Ca_2^+ has a $(\sigma_{4s})^2 (\sigma^\star_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

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9.8: Second-Row Diatomic Molecules

Learning Objectives

- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character. We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2.

four key points to remember when drawing molecular orbital diagrams:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the "*law of conservation of orbitals*").
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure $9.8.1$; the n = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the n = 2 level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^{\star}_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of (8 – 6) ÷ 2 = 1. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

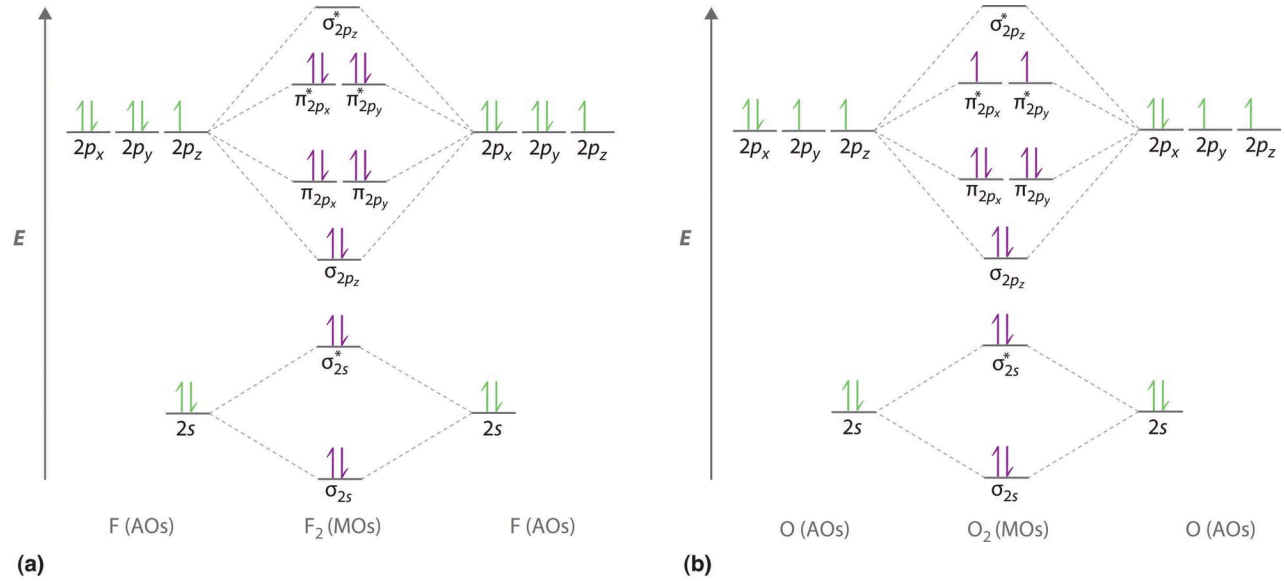


Figure 9.8.1: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_x},\ \pi^*_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure 9.8.1. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and $\sigma_{2s}{}^*$ orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of (8 – 4) ÷ 2 = 2, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure 9.8.2, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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Figure 9.8.2: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because

Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^*_{np_x}$ and $\pi^*_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 9.8.3 Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 9.8.3). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

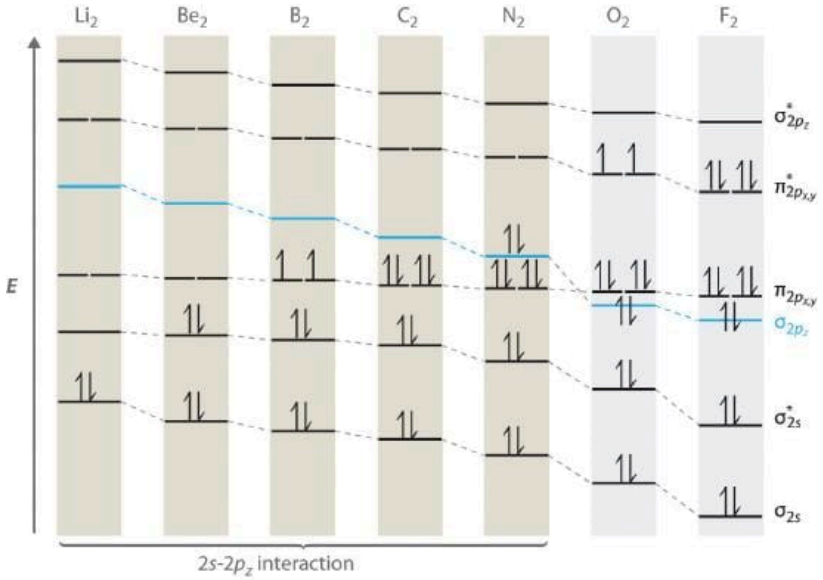


Figure 9.8.3: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is *lower* in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row.

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

Example 9.8.3: Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

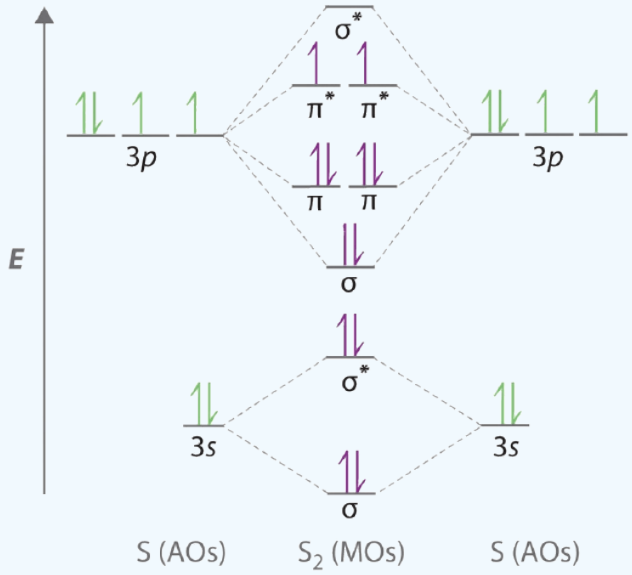
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a [Ne]$3s^2 3p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure 9.8.1 and Figure 9.8.3, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure 9.8.3), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Two filled sigma orbitals, one filled sigma * orbital, two filled pi orbitals, and two pi * orbitals with one unpaired electron.

Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_x}$ and $\pi^*_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2 (\sigma^*_{3s})^2 (\sigma_{3p_z})^2 (\pi_{3p_{x,y}})^4 (\pi^*_{3p_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 – 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 9.8.3: The Peroxide Ion

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer available at the end of this section.

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 9.8.4. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

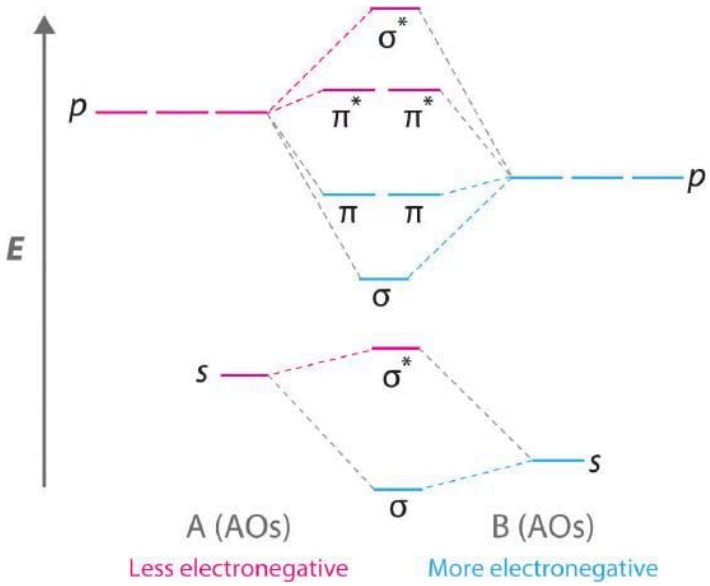


Figure 9.8.4: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 9.8.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 9.8.11). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

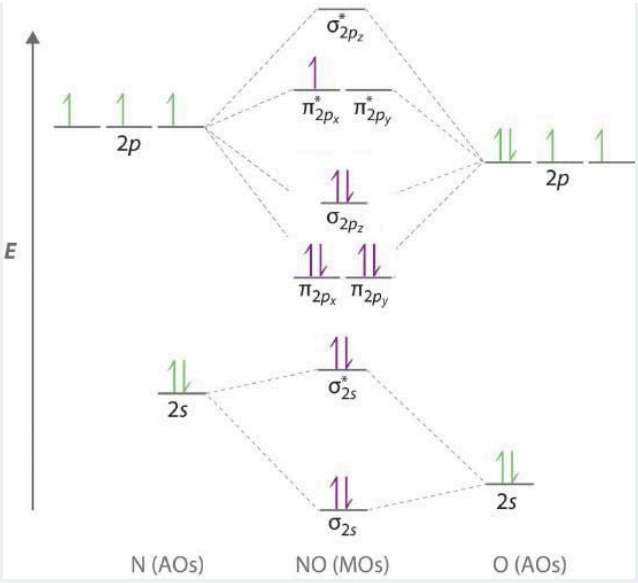


Figure 9.8.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_z},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\,(\sigma^{\star}_{2s})^2\,\left(\pi_{2p_{x,y}}\right)^4\,(\sigma_{2p_z})^2\,\left(\pi_{2p^{\star}_{x,y}}\right)^1$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the NO molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure 9.8.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 9.8.13, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 9.8.6 that the 1s orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3s atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1s and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1s orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1s orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3s, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 – 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1s atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}--Cl^{\delta-}$.

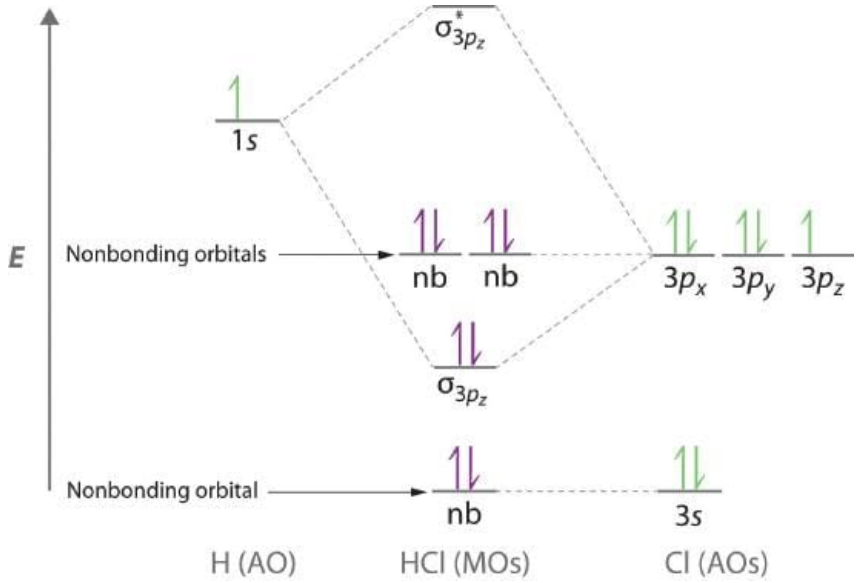


Figure 9.8.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

Electrons in nonbonding molecular orbitals have no effect on bond order.

Example 9.8.4: The Cyanide Ion

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 9.8.4 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

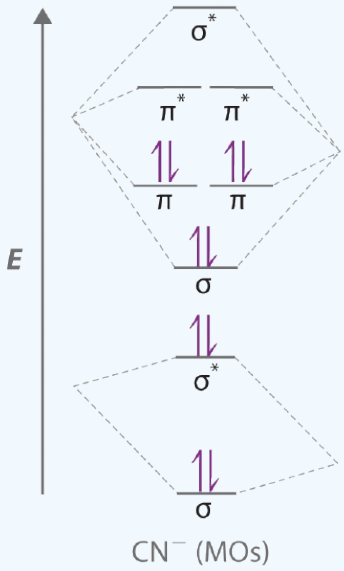
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 9.8.4 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the –1 charge. Placing these electrons in an energy-level diagram like Figure 9.8.4 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of (8 – 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

Exercise 9.8.4: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer available at the end of this section.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

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Summary

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional

to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise $9.8.3$**: The Peroxide Ion**

$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p_z})^2 (\pi_{2p_{x,y}})^4 (\pi_{2p^*_{x,y}})^4$ bond order of 1; no unpaired electrons

Exercise $9.8.4$**: The Hypochlorite Ion**

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

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9.E: Exercises

9.1: MOLECULAR SHAPES

9.2: THE VSEPR MODEL

Conceptual Problems

1. What is the main difference between the VSEPR model and Lewis electron structures?
2. What are the differences between molecular geometry and Lewis electron structures? Can two molecules with the same Lewis electron structures have different molecular geometries? Can two molecules with the same molecular geometry have different Lewis electron structures? In each case, support your answer with an example.
3. How does the VSEPR model deal with the presence of multiple bonds?
4. Three molecules have the following generic formulas: AX_2, AX_2E, and AX_2E_2. Predict the molecular geometry of each, and arrange them in order of increasing X–A–X angle.
5. Which has the smaller angles around the central atom—H_2S or SiH_4? Why? Do the Lewis electron structures of these molecules predict which has the smaller angle?
6. Discuss in your own words why lone pairs of electrons occupy more space than bonding pairs. How does the presence of lone pairs affect molecular geometry?

- When using VSEPR to predict molecular geometry, the importance of repulsions between electron pairs decreases in the following order: LP–LP, LP–BP, BP–BP. Explain this order. Draw structures of real molecules that separately show each of these interactions.
- How do multiple bonds affect molecular geometry? Does a multiple bond take up more or less space around an atom than a single bond? a lone pair?
- Straight-chain alkanes do not have linear structures but are “kinked.” Using *n*-hexane as an example, explain why this is so. Compare the geometry of 1-hexene to that of *n*-hexane.
- How is molecular geometry related to the presence or absence of a molecular dipole moment?
- How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?
- What two features of a molecule’s structure and bonding are required for a molecule to be considered polar? Is COF_2 likely to have a significant dipole moment? Explain your answer.
- When a chemist says that a molecule is *polar*, what does this mean? What are the general physical properties of polar molecules?
- Use the VSPER model and your knowledge of bonding and dipole moments to predict which molecules will be liquids or solids at room temperature and which will be gases. Explain your rationale for each choice. Justify your answers.

    1. CH_3Cl
    2. PCl_3
    3. CO
    4. SF_6
    5. IF_5

6. CH_3OCH_3
7. CCl_3H
8. H_3COH

- The idealized molecular geometry of BrF_5 is square pyramidal, with one lone pair. What effect does the lone pair have on the actual molecular geometry of BrF_5? If LP–BP repulsions were *weaker* than BP–BP repulsions, what would be the effect on the molecular geometry of BrF_5?
- Which has the smallest bond angle around the central atom—H_2S, H_2Se, or H_2Te? the largest? Justify your answers.
- Which of these molecular geometries *always* results in a molecule with a net dipole moment: linear, bent, trigonal planar, tetrahedral, seesaw, trigonal pyramidal, square pyramidal, and octahedral? For the geometries that do not always produce a net dipole moment, what factor(s) will result in a net dipole moment?

Conceptual Answers

1.
2.
3. To a first approximation, the VSEPR model assumes that multiple bonds and single bonds have the same effect on electron pair geometry and molecular geometry; in other words, VSEPR treats multiple bonds like single bonds. Only when considering fine points of molecular structure does VSEPR recognize that multiple bonds occupy more space around the central atom than single bonds.
4.
5.
6.
7.
8.
9.
10.
11. Physical properties like boiling point and melting point depend upon the existence and magnitude of the dipole moment of a molecule. In general, molecules that have substantial dipole moments are likely to exhibit greater intermolecular interactions, resulting in higher melting points and boiling points.
12.
13. The term “polar” is generally used to mean that a molecule has an asymmetrical structure and contains polar bonds. The resulting dipole moment causes the substance to have a higher boiling or melting point than a nonpolar substance.

Numerical Problems

1. Give the number of electron groups around the central atom and the molecular geometry for each molecule. Classify the electron groups in each species as bonding pairs or lone pairs.
    1. BF_3
    2. PCl_3
    3. XeF_2
    4. $AlCl_4^-$
    5. CH_2Cl_2
2. Give the number of electron groups around the central atom and the molecular geometry for each species. Classify the electron groups in each species as bonding pairs or lone pairs.
    1. ICl_3
    2. CCl_3^+

3. H_2Te
4. XeF_4
5. NH_4^+

3. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

    1. HCl
    2. NF_3
    3. ICl_2^+
    4. N_3^-
    5. H_3O^+

4. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

    1. SO_3
    2. NH_2^-
    3. NO_3^-
    4. I_3^-
    5. OF_2

5. What is the molecular geometry of ClF_3? Draw a three-dimensional representation of its structure and explain the effect of any lone pairs on the idealized geometry.

6. Predict the molecular geometry of each of the following.

    1. ICl_3
    2. AsF_5
    3. NO_2^-
    4. $TeCl_4$

7. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

    1. NO
    2. HF
    3. PCl_3
    4. CO_2
    5. SO_2
    6. SF_4

8. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

    1. OF_2
    2. BCl_3
    3. CH_2Cl_2
    4. TeF_4
    5. CH_3OH
    6. XeO_4

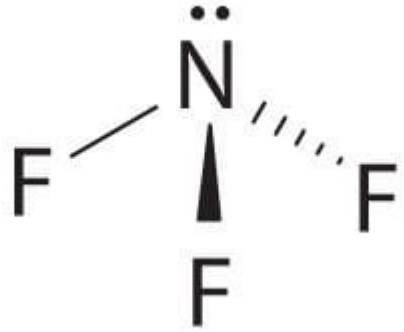
9. Of the molecules $Cl_2C{=}Cl_2$, IF_3, and SF_6, which has a net dipole moment? Explain your reasoning.

10. Of the molecules SO_3, XeF_4, and $H_2C{=}Cl_2$, which has a net dipole moment? Explain your reasoning.

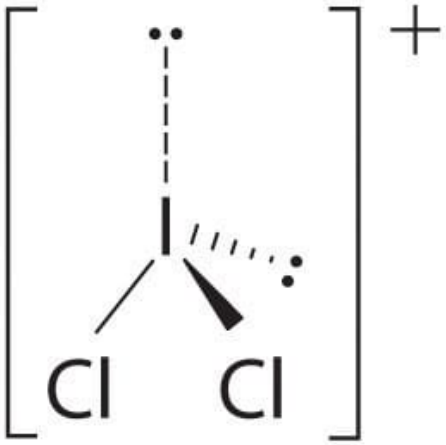
Numerical Answers

1. 1. trigonal planar (all electron groups are bonding pairs)
   2. tetrahedral (one lone pair on P)
   3. trigonal bipyramidal (three lone pairs on Xe)
   4. tetrahedral (all electron groups on Al are bonding pairs)
   5. tetrahedral (all electron groups on C are bonding pairs)
2.
3. 1. four electron groups, linear molecular geometry

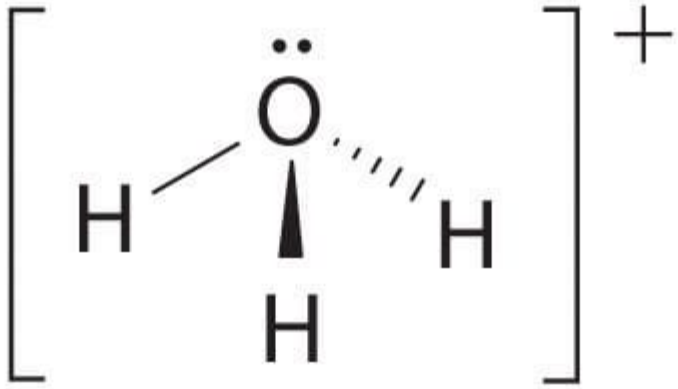
   2. four electron groups, pyramidal molecular geometry

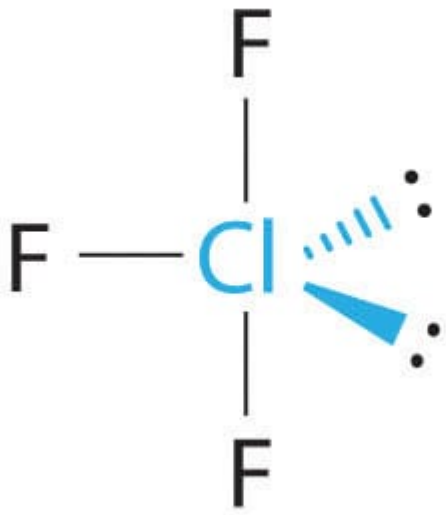


   3. four electron groups, bent molecular geometry



   4. two electron groups, linear molecular geometry
   5. four electron groups, pyramidal molecular geometry

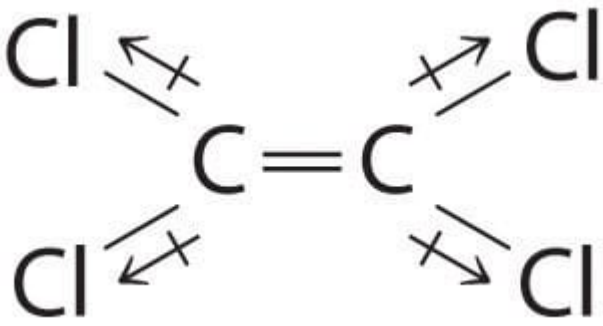
4. 

5. 

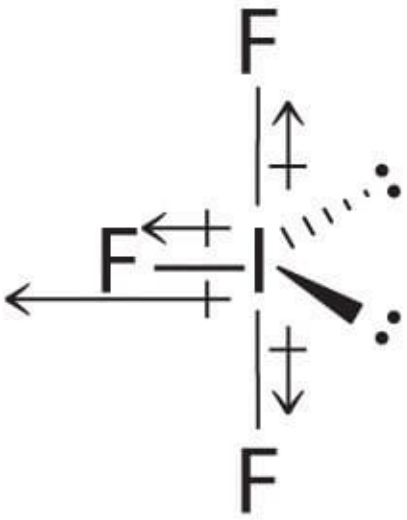
   The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F–Cl–F angle *less* than 180°.

6.
7.
8.

9. $Cl_2C{=}CCl_2$: Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.



   IF_3: In this structure, the individual I–F bond dipoles cannot cancel one another, giving IF_3 a net dipole moment.



SF_6: The S–F bonds are quite polar, but the individual bond dipoles cancel one another in an octahedral structure. Thus, SF_6 has no net dipole moment.



9.3: MOLECULAR SHAPE AND MOLECULAR POLARITY

Conceptual Problems

1. Why do ionic compounds such as KI exhibit substantially less than 100% ionic character in the gas phase?
2. Of the compounds LiI and LiF, which would you expect to behave more like a classical ionic compound? Which would have the greater dipole moment in the gas phase? Explain your answers.

Numerical Problems

1. Predict whether each compound is purely covalent, purely ionic, or polar covalent.

    1. RbCl
    2. S_8
    3. $TiCl_2$

4. $SbCl_3$
5. LiI
6. Br_2

2. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.

   1. NO
   2. HF
   3. MgO
   4. $AlCl_3$
   5. SiO_2
   6. the C=O bond in acetone
   7. O_3

3. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.

   1. NaBr
   2. OF_2
   3. BCl_3
   4. the S–S bond in $CH_3CH_2SSCH_2CH_3$
   5. the C–Cl bond in CH_2Cl_2
   6. the O–H bond in CH_3OH
   7. $PtCl_4^{2-}$

4. Classify each species as having 0%–40% ionic character, 40%–60% ionic character, or 60%–100% ionic character based on the type of bonding you would expect. Justify your reasoning.

   1. CaO
   2. S_8
   3. $AlBr_3$
   4. ICl
   5. Na_2S
   6. SiO_2
   7. LiBr

5. If the bond distance in HCl (dipole moment = 1.109 D) were double the actual value of 127.46 pm, what would be the effect on the charge localized on each atom? What would be the percent negative charge on Cl? At the actual bond distance, how would doubling the charge on each atom affect the dipole moment? Would this represent more ionic or covalent character?

6. Calculate the percent ionic character of HF (dipole moment = 1.826 D) if the H–F bond distance is 92 pm.

7. Calculate the percent ionic character of CO (dipole moment = 0.110 D) if the C–O distance is 113 pm.

8. Calculate the percent ionic character of PbS and PbO in the gas phase, given the following information: for PbS, r = 228.69 pm and μ = 3.59 D; for PbO, r = 192.18 pm and μ = 4.64 D. Would you classify these compounds as having covalent or polar covalent bonds in the solid state?

9.4: COVALENT BONDING AND ORBITAL OVERLAP

9.5: HYBRID ORBITALS

Conceptual Problems

1. Arrange sp, sp^3, and sp^2 in order of increasing strength of the bond formed to a hydrogen atom. Explain your reasoning.

2. What atomic orbitals are combined to form sp^3, sp, sp^3d^2, and sp^3d? What is the maximum number of electron-pair bonds that can be formed using each set of hybrid orbitals?

3. Why is it incorrect to say that an atom with sp^2 hybridization will form only three bonds? The carbon atom in the carbonate anion is sp^2 hybridized. How many bonds to carbon are present in the carbonate ion? Which orbitals on carbon are used to form each bond?

4. If hybridization did not occur, how many bonds would N, O, C, and B form in a neutral molecule, and what would be the approximate molecular geometry?

5. How are hybridization and molecular geometry related? Which has a stronger correlation—molecular geometry and hybridization or Lewis structures and hybridization?

6. In the valence bond approach to bonding in BeF_2, which step(s) require(s) an energy input, and which release(s) energy?

7. The energies of hybrid orbitals are intermediate between the energies of the atomic orbitals from which they are formed. Why?

8. How are lone pairs on the central atom treated using hybrid orbitals?

9. Because nitrogen bonds to only three hydrogen atoms in ammonia, why doesn't the nitrogen atom use sp^2 hybrid orbitals instead of sp^3 hybrids?

10. Using arguments based on orbital hybridization, explain why the CCl_6^{2-} ion does not exist.

11. Species such as NF_5^{2-} and OF_4^{2-} are unknown. If $3d$ atomic orbitals were much lower energy, low enough to be involved in hybrid orbital formation, what effect would this have on the stability of such species? Why? What molecular geometry, electron-pair geometry, and hybridization would be expected for each molecule?

Numerical Problems

1. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^-. How does your diagram compare with that for methane? What is the molecular geometry?

2. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^+. How does your diagram compare with that for methane? What is the molecular geometry?

3. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each molecule.

    1. BBr_3
    2. PCl_3
    3. NO_3^-

4. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each species.

    1. $AsBr_3$
    2. CF_3^+
    3. H_2O

5. What is the hybridization of the central atom in each of the following?

    1. CF_4
    2. CCl_2^{2-}
    3. IO_3^-
    4. SiH_4

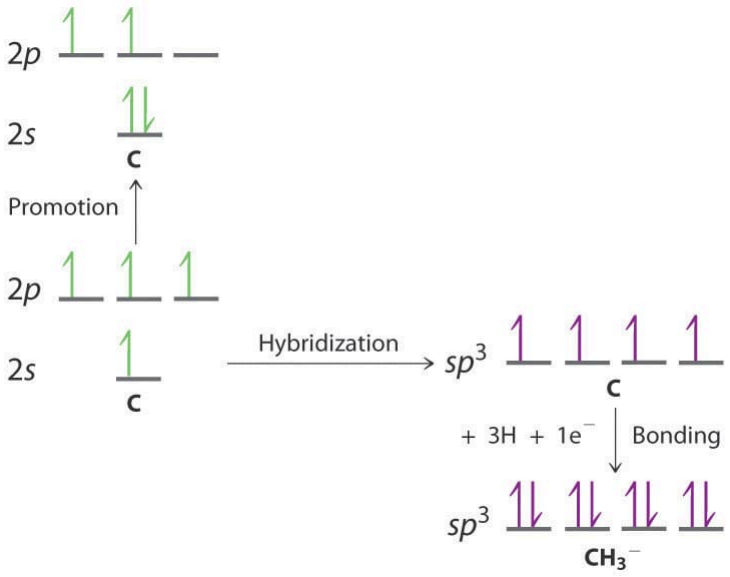
6. What is the hybridization of the central atom in each of the following?

    1. CCl_3^+
    2. CBr_2O
    3. CO_3^{2-}
    4. IBr_2^-

7. What is the hybridization of the central atom in PF_6^-? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

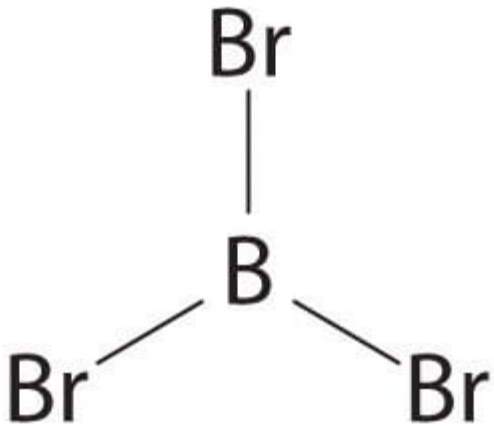
8. What is the hybridization of the central atom in SF_5^-? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

Numerical Answers

1. 

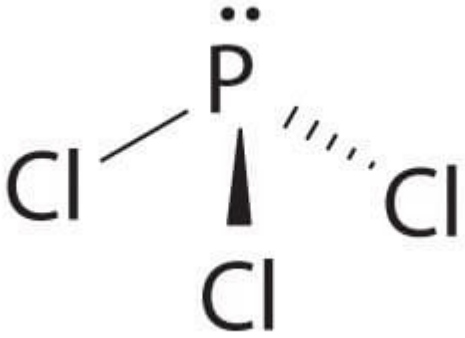
    The promotion and hybridization process is exactly the same as shown for CH_4 in the chapter. The only difference is that the C atom uses the four singly occupied sp^3 hybrid orbitals to form electron-pair bonds with only *three* H atoms, and an electron is added to the fourth hybrid orbital to give a charge of 1–. The electron-pair geometry is tetrahedral, but the molecular geometry is pyramidal, as in NH_3.

2.



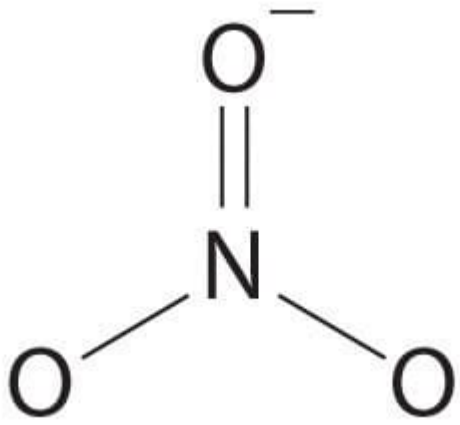
3. 1.

   sp^2, trigonal planar



2.

   sp^3, pyramidal



3.

   sp^2, trigonal planar

4.

5. The central atoms in CF_4, CCl_2^{2-}, IO_3^-, and SiH_4 are all sp^3 hybridized.

6.

7. The phosphorus atom in the PF_6^- ion is sp^3d^2 hybridized, and the ion is octahedral. The PF_6^- ion is isoelectronic with SF_6 and has essentially the same structure. It should therefore be a stable species.

9.6: MULTIPLE BONDS

Conceptual Problems

1. What information is obtained by using the molecular orbital approach to bonding in O_3 that is not obtained using the VSEPR model? Can this information be obtained using a Lewis electron-pair approach?
2. How is resonance explained using the molecular orbital approach?
3. Indicate what information can be obtained by each method:

	Lewis Electron Structures	VSEPR Model	Valence Bond Theory	Molecular Orbital Theory
Geometry				
Resonance				
Orbital Hybridization				
Reactivity				
Expanded Valences				
Bond Order				

Numerical Problems

1. Using both a hybrid atomic orbital and molecular orbital approaches, describe the bonding in BCl_3 and CS_3^{2-}.
2. Use both a hybrid atomic orbital and molecular orbital approaches to describe the bonding in CO_2 and N_3^-.

9.7: MOLECULAR ORBITALS

9.8: SECOND-ROW DIATOMIC MOLECULES

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9.S: Molecular Geometry and Bonding Theories (Summary)

9.1: Molecular Shapes

The Lewis electron-pair approach described previously can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however.

- **Bond angles**: angles made by the lines joining the nuclei of the atoms in a molecule
- Bond angles determine overall shape of molecule

VSEPR Model" data-cke-saved-href="/Bookshelves/General_Chemistry/Map:_Chemistry_-_The_Central_Science_(Brown_et_al.)/09:_Molecular_Geometry_and_Bondin 9.02:_The_VSEPR_Model" href="/Bookshelves/General_Chemistry/Map:_Chemistry_-_The_Central_Science_(Brown_et_al.)/09:_Molecular_Geometry_and_Bondin 9.02:_The_VSEPR_Model" data-quail-id="12">9.2: The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The VSEPR model is not a theory; it does not attempt to explain observations. Instead, it is a counting procedure that accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

The Valence-Shell Electron Pair-Repulsion Model

- *Valence-shell electron-pair repulsion (VSEPR) model:* model that accounts for the geometric arrangements of shared and unshared electron pairs around a central atom in terms of the repulsions between electron pairs
- Electrons repel one another; hence, *the best arrangement of a given number of electron pairs is the one that minimizes the repulsions among them.*

Predicting Molecular Geometries

- Two types of valence-shell electron pairs; *bonding pairs* and *nonbonding pairs*.
- **Electron-pair geometry**: 3-D arrangement of electron pairs around an atom according to the VSEPR model
- **Molecular geometry**: the arrangement in space of the atoms of a molecule

When describing the shapes of molecules, we always give the *molecular* geometry rather than the *electron-pair* geometry. Molecular geometries only include BONDING pairs. For example, NH_3 is a tetrahedral according to electron-pair geometry because it has 3 bonds and an unshared pair of electron. However, according to molecular geometry it is a trigonal pyramidal because it has only 3 bonds.

How to predict molecular geometries using VSEPR model:

1. Sketch the Lewis dot structure of the molecule or ion
2. Count the total number of electron pairs around the central atom and arrange them in the way that minimizes electron-pair repulsions
3. Describe the molecular geometry in terms of the angular arrangement of the *bonding* pairs

Four or Fewer Valence-Shell Electron Pairs

A double or triple bond has essentially the same effect on bond angles as a single bond and is therefore counted as one bonding pair (that is, one electron region) when predicting geometry

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

Bond angles decrease as the number of nonbonding electron pairs increases. Bonding pairs are attracted by the two nuclei. By contrast, nonbonding electrons move under the attractive influence of only one nucleus and thus spread out more in space.

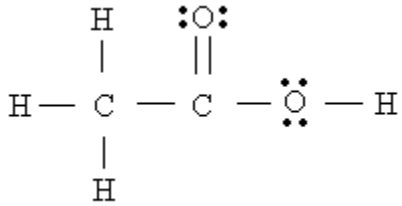
- *Nonbonding electron pairs exert greater repulsive forces on adjacent electron pairs and thus tend to compress the angles between the bonding pairs*
- *Electrons in multiple bonds, like nonbonding pairs, exert a greater repulsive force on adjacent electron pairs than do single bonds.*

Geometries of Molecules with Expanded Valence Shells

- When the central atom of a molecule or ion is from the third period of the periodic table and beyond (has *d* subshell) that atom may have more than four electron pairs around it
- The most stable electron-pair geometry for five electron pairs is the Trigonal bipyramid.
- Trigonal bipyramid geometries have two distinct types of electron pairs. They are *axial pairs* and *equatorial pairs*. In axial position, an electron pair is situated 90° from the three equatorial pairs. In an equatorial position, an electron pairs is situated 120° from the other two equatorial pairs and 90° from the two axial pairs.
- Because nonbonding pairs exert larger repulsions than bonding pairs, they always occupy the equatorial positions
- The most stable electron-pair geometry for six electron pairs is the *octahedron*.
- In an octahedron, the angles are either 90° or 180°, and all six positions are equivalent

Molecules with No Single Central Atom

Consider acetic acid molecule



Carbon bonded to three hydrogens and one carbon. Second carbon is double bonded to one oxygen and single bonded to another oxygen. The single bonded oxygen is bonded to a hydrogen.

- Notice that the leftmost C has four bonded pairs around it. Hence, it must be a tetrahedral.
- The central C has 3 bonding pairs around it (counting the double bond as a single pair), hence, it is trigonal planar
- O has two bonding pairs, and two nonbonding ones. Hence, it is bent.

9.3: Molecular Shape and Molecular Polarity

Compounds with polar covalent bonds have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a dipole moment, which is the product of the partial charges on the bonded atoms and the distance between them.

Polar: in a molecule, if its centers of negative and positive charge don't coincide, aka **dipole**

- If there are no charges on the opposite ends of a molecule, or if the charges have the same sign, the molecule does not have a dipole moment and is therefore *nonpolar*. Any diatomic molecule with a polar bond is a polar molecule
- Polar molecules align themselves with respect to one another. The negative end of a polar molecule is attracted to a positive ion, the positive end is attracted to a negative ion
- **Dipole moment**: measures the degree of polarity of a given molecule. The dipole moment, μ, is the product of the charge at either end of the dipole, Q, times the distance, r, between the charges.

$$\mu = Qr$$

Therefore, the dipole moment increases as the quantity of charge that is separated increases and as the distance between the positive and negative centers increases. Dipole moments are generally reported in debyes (D), a unit equaling 3.33 X 10^{-30} C-m.

The Polarity of Polyatomic Molecules

- The polarity of a molecule containing more than two atoms depends on both the polarities of the bonds and the geometry of the molecule
- For each polar bond in a molecule, we can consider the *bond dipole,* that is, the dipole moment due only to the two atoms bonded together. We must then ask what the overall dipole moment results from adding up the individual bond dipoles. Let's use CO_2 (linear) as an example
- In CO_2, each C – O bond is polar, and because they are identical, the bond dipoles are equal in magnitude.
- The fact that both C – O bonds are polar doesn't necessarily mean the whole CO_2 molecule is
- Bond dipoles and dipole moments are vector quantities; they have both a magnitude and direction. When calculating the overall dipole moment, both the magnitude and direction of the bond dipoles must be considered in this sum of vectors
- The two bond dipoles in CO_2, although equal in magnitude, are opposite in direction, which makes them cancel each other out. Hence, CO_2 has an overall dipole moment of zero. Even though the oxygen atoms in CO_2 carry a partial negative charge, the geometry of the molecule dictates the overall dipole moment.
- Now, let's consider H_2O. Both of its bonds are identical once again, but the geometry is bent instead of linear. Hence, the bonds do not cancel each other out, and H_2O has a dipole moment
- Molecules in which the central is symmetrically surrounded by identical atoms (BF_3, CCl_4) are nonpolar.
- For AB_n molecules in which ALL of the B atoms are the same, certain symmetrical geometries – linear (AB_2), trigonal planar (AB_3), tetrahedral and square planar (AB_4), trigonal bipyramidal (AB_5), and octahedral (AB_6) – must lead to nonpolar molecules, regardless of how polar the individual bonds are.

9.4: Covalent Bonding and Orbital Overlap

A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called hybridization, which results in the formation of stronger bonds.

Valence bond theory: model of chemical bonding in which an electron-pair bond is formed between two atoms by the overlap of orbitals on the two atoms

- Covalent bonding occurs when atoms share electrons. This increases the electron density between the two nuclei, and is visualized as occurring when a valence atomic orbital of one atom merges with that of another atom
- As the distance between the atoms decreases, their overlap increases. Because of the resultant increase in electron density between the nuclei, the potential energy of the system decreases, increasing the strength of the bond.
- The observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) are balanced by the repulsive forces between like charges (electron-electron and nucleus-nucleus)

9.5: Hybrid Orbitals

The localized valence bonding theory uses a process called hybridization, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (hybridizing) two or more atomic orbitals from the same atom.

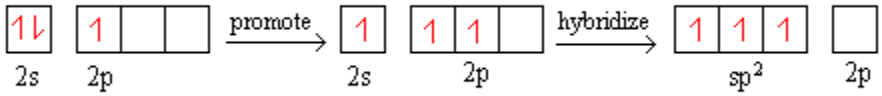
sp Hybrid Orbitals

- Use the salt BeF_2 as an example. Its geometry is linear, however it is now hard to determine which orbitals on the Be atom overlap with those of the F atoms. The electron configuration of Be is $1s^2$ $2s^2$. Hence, Be in its ground state has no unpaired electrons and is unable to form bonds
- Be's only option is to "promote" one of its two electrons in the 2s shell to the 2p shell. It will then have a configuration of $1s^2$

$2s^1\ 2p^1$. Since the 2p orbital is at a higher energy level than the 2s orbital, this promotion requires energy
- The Be atom now has two unpaired electrons (2s and 2p) and would be able to form two bonds, which will not be similar. The two new orbitals are identical in shape (two lobes; one much larger than the other) but are oriented in different directions. Two hybrid orbitals have been created
- **Hybrid orbitals**: orbitals that result from the mixing of different kinds of atomic orbitals on the same atom. For example and sp^3 hybrid results from the mixing, or hybridizing, of one *s* orbital and three *p* orbitals
- **Hybridization**: mixing of different types of atomic orbitals to produce a set of equivalent hybrid orbitals
- In this case, we have hybridized one *s* and one *p* orbital, so we call each hybrid an *sp hybrid orbital*. For the Be atom of BeF_2, the orbital diagram is written as follows: $1s^2\ 2sp^2$
- Hybrid orbitals have one large lobe and can therefore be directed at surrounding atoms more effectively, forming stronger bonds. The energy released by such bonds enables the promotion of a 2s electron to the 2p level.

sp^2 and sp^3 Hybrid Orbitals

- Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals. Each of these hybrid orbitals is equivalent to the others but points in a different direction.
- Consider BF_3. B has an electron configuration of $2s^2\ 2p^1$. It promotes one of its 2s electron to the 2p orbital to have a configuration of $2s^1\ 2p^2$. Then, it hybridizes into 3 sp^2 hybrid orbitals



The same process can apply to the creation of sp^3 hybrid orbitals

Hybridization Involving *d* Orbitals

Same process as sp^2 orbitals. For example, mixing one *s* orbital, three *p* orbitals, and two *d* orbitals gives six sp^3d^2 hybrid orbitals, which are directed at the vertices of an octahedron

Section Summary

The molecular geometry needs to be known first in order to use the concept of hybridization, then we can use the following rules:

1. Draw the Lewis structure for the molecule or ion
2. Determine the electron-pair geometry using the VSEPR model
3. Specify the hybrid orbitals needed to accommodate the electron pairs based on their geometrical arrangement

9.6: Multiple Bonds

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σσ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized np orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations.

In each covalent bond we have considered so far, the electron density is concentrated symmetrically about the line that connects the two nuclei (*internuclear axis*). This axis passes through the middle of the overlap region

- **Sigma (σ) bond**: covalent bond in which electron density is concentrated along the internuclear axis
- **Pi (π) bond**: covalent bond in which electron density is concentrated above and below the internuclear axis. Pi bonds are generally weaker than sigma bonds (less overlap)

Usually, single bonds are σ bonds. A double bond has one σ bond and one π bond. A triple bond has one σ bond and two π bonds.

Consider C_2H_4 as an example. After hybridization, C has 3 sp^2 hybrid orbitals and one electron in the remaining unhybridized 2p

orbital. The unhybridized 2p electron is directly perpendicular to the plane that contains the three sp^2 hybrid orbitals

- The C – H σ bond is formed by the overlap of a sp^2 hybrid orbital with the 1s orbital of hydrogen. Hence, the bond uses two electrons
- The C – C σ bond is formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom, and requires two more electrons. Overall, C_2H_4 has 12 valence electrons, 10 of which are used in the formation of the bonds
- The remaining two valence electrons reside in the unhybridized 2p orbitals, one electron on each of the atoms
- The 2p orbitals can overlap with one another in a sideways fashion. This will lead to the electron density being concentrated above and below the C – C bond axis, hence being a π bond

Because π bonds require that portions of a molecule be planar, they can introduce rigidity into molecules (strongly affects the properties of substances)

Although π bonds can be formed from *d* orbitals, we will only consider those formed by *p* orbitals. They can only form if unhybridized *p* orbitals are present on the bonded atoms. Only atoms having *sp* or sp^2 hybridization can be involved in π bonding. Double and triple bonds are more common in molecules with small atoms

Delocalized Bonding

- σ and π electrons are *localized* when they are associated totally with two atoms forming the bond.
- In some molecules, particularly those with more than one resonance form, we cannot accurately describe the bonding as localized. In order to deal with this, we "smear out" the bonds (*delocalize* them) so that it fits both resonance structures as best as possible

Delocalized electrons: electrons that are spread over a number of atoms in a molecule rather than localized between a pair of atoms

Section Summary

1. Every pair of bonded atoms shares one or more pairs of electrons. In every bond, at least one pair of electrons is localized in the space between the atoms, in a σ bond. The appropriate set of hybrid orbitals used to form the σ bonds between an atom and its neighbors is determined by the observed geometry of the molecule
2. The electrons in σ bonds are localized in the region between two bonded atoms and do not make a significant contributions to the bonding between any other two atoms
3. When atoms share more than one pair of electrons, the additional pairs are in π bonds. The centers of chare density in a π bond lie above an below the bond axis.
4. Molecules with two or more resonance forms can have π bonds that extend over more than two bonded atoms. Electrons in π bonds that extend over more than two bonded atoms are said to be delocalized

9.7: Molecular Orbitals

A molecular orbital is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital, which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the molecular orbital theory of bonding is a delocalized approach. Molecular orbitals are constructed using linear combinations of atomic orbitals (LCAOs), which describe overlapping atomic orbitals.

- **Molecular orbital theory**: theory that predicts that electrons in molecules exist in allowed energy states.
- **Molecular orbitals**: allowed state for an electron in a molecule. Molecular orbitals are very similar to atomic orbitals. Both hold a maximum of two electrons (with opposite spins), have definite energies, and their electron-density distribution can be visualized by using contour representations. However, molecular orbitals are associated with the *entire* molecule

The Hydrogen Molecule

Consider H_2 as an example. Whenever two atomic orbitals overlap, two molecular orbitals form. Thus, the overlap of the 1s orbitals of two hydrogen atoms to form H_2 produces two molecular orbitals.

Bonding molecular orbital: molecular orbital in which the electron density is concentrated in the internuclear region. The energy

of a bonding molecular orbital is lower than the energy of the separate atomic orbitals from which it forms.

The bonding molecular orbital results from summing the two atomic orbitals so that the atomic orbital wave functions enhance each other in the bond region. Because an electron in this molecular orbital is strongly attracted to both nuclei, the electron is more stable (lower energy) than it is in the 1s orbital of hydrogen. Because it concentrates electron density between both nuclei, the bonding molecular orbital holds the atoms together in a covalent bond.

Antibonding molecular orbital: molecular orbital in which electron density is concentrated outside the region between the two nuclei of bonded atoms. Such orbitals, designated as σ* or π*, are less stable (of higher energy) than bonding molecular orbitals

- An electron in the antibonding molecular orbital is repelled from the bonding region and is therefore less stable (higher energy) than it is in the 1s orbital of the hydrogen atom
- **Sigma (σ) molecular orbital**: molecular orbital that centers the electron density about an imaginary line passing through two nuclei
- **Energy level diagram**: aka **Molecular orbital diagram**; diagram that shows the energies of molecular orbitals relative to the atomic orbitals from which they are derived
- Electrons occupying a bonding molecular orbital are called *bonding* electrons

Bond Order

- **Bond order**: related to the stability of a covalent bond.

$$\text{Bond order} = \frac{1}{2}(\text{number of bonding electrons} - \text{number of antibonding electrons})$$

A bond order of 1 represents a single bond, a bond order of 2 represents a double bond, and a bond order of 3 represents a triple bond. A bond order of 0 means that no bonds exist

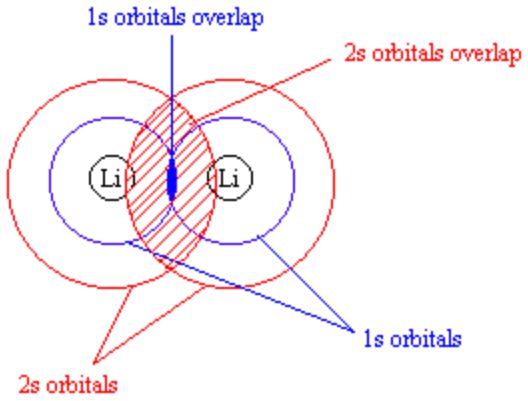
9.8: Second-Row Diatomic Molecules

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the atomic orbitals increases.

Material here applies to *homonuclear* diatomic molecules (those composed of identical atoms)

1. The number of atomic orbitals formed equals the number of atomic orbitals combined
2. Atomic orbitals combine most effectively with other atomic orbitals of similar energy
3. The effectiveness with which two atomic orbitals combine is proportional to their overlap with one another; that is, as the overlap increases, the bonding orbital is lowered in energy, and the antibonding orbital is raised in energy
4. Each molecular orbital can accommodate at most two electrons, with their spins paired (Pauli exclusion principle)
5. When molecular orbitals have the same energy, one electron enters each orbital (with parallel spins) before spin pairing occurs (Hund's rule)

Molecular Orbitals for Li_2 and Be_2



The 2 s orbitals are drawn in red whild the 1 s orbitals are drawn in blue. There is an overlap between the two 1 s orbitals and two 2 s orbitals.

- Lithium has 1s and 2s orbitals, but both are extremely different. According to the Lewis structure of Li_2, there is a single Li – Li bond.
- Because the 1s and 2s orbitals are so different in energy, it is likely that the 1s orbitals interact with each other. (See rule 2)
- This would create a much larger overlap between the 2s orbitals (see figure)
- As a result, the energy seperation between the σ_{2s} and σ^*_{2s} is greater than that for the 1s-based orbitals.
- Each Li atom has 3 electrons; so six electrons must be placed in the molecular orbitals of Li_2
- The electrons occupy the σ_{1s} , σ^*_{1s} , and σ_{2s} orbitals (not the σ^*_{2s} orbital). There are 4 bonding orbitals and 2 nonbonding ones, so the bond order equals ½ (4 – 2) = 1. The molecule has a single bond, in accord with its Lewis structure.

Filled atomic subshells usually do not contribute significantly to bonding in molecule formation

In Be_2, each Be has 4 electrons, for a total of eight. When we place them in molecular orbitals, we fill the σ_{1s} , σ^*_{1s} , σ_{2s} , and σ^*_{2s} orbitals. There is an equal number of bonding and antibonding electrons, so the bond order is 0. Thus, Be_2 doesn't exist.

Molecular Orbitals from *2p* Atomic Orbitals

- *z* axis is internuclear axis (in this example). $2p_z$ orbitals face each other in a "head-to-head" fashion along the *z*-axis. They combine like the s orbitals, with one combination concentrating electron density between both nuclei, and the other excluding the electron density from the bonding region. In each of these combinations, the electron density lies along the internuclear axis. Hence, they are σ molecular orbitals: σ_{2p} and σ^*_{2p}
- The other 2p orbitals overlap in a sideways fashion and thus concentrate electron density on opposite sides of the internuclear axis. Molecular orbitals of this type are called **pi molecular orbitals** . We get two π_{2p} molecular orbitals by combining $2p_x$ and $2p_y$ molecular orbitals. The resulting π_{2p} molecular orbitals are degenerate (same energy). Likewise, two degenerate π^*_{2p} antibonding molecular orbitals are formed.
- The $2p_z$ orbitals on two atoms point directly at one another, hence, having a greater overlap than the $2p_x$ and $2p_y$ orbitals. From rule 3, we can expect the σ_{2p} molecular orbital to be lower in energy (more stable) tha n the π_{2p} molecular orbitals.

Electron Configurations for B_2 Through F_2

- The elements Boron through Fluorine all have 2s and 2p valence electrons
- In the energy diagram, the σ_{2p} molecular orbital is at higher energy than the π_{2p} molecular orbitals, contrary to what we would expect from rule 3.
- This is because of interaction between the σ_{2s} and σ_{2p} molecular orbitals. It results in the σ_{2p} molecular orbital being pushed upward in energy to the point where it is above the π_{2p} orbi tals, and the σ_{2s} molecular orbital is pushed down in energy. (The interaction between σ_{2p} and σ_{2s} molecular orbitals decreases as we move from left to right in the second period. As a result, the σ_{2p} is higher in energy than the π_{2p} orbitals for B_2, C_2, and N_2. For O_2, F_2, and Ne_2 , the σ_{2p} orbital is lower in energy than the π_{2p} orbitals)
- Boron has 3 valence electrons. Thus, for B_2, we must place 6 electrons in molecular orbitals. Four of these occupy the σ_{2s} and σ^*_{2s} molecular orbitals, leading to no net bonding. The last two electrons are put in the π_{2p} bonding molecular orbitals; one electron is put in each π_{2p} molecular orbital with the same spin (rule 5). Therefore, B_2 has a bond order of 1.

Electron Configurations and Molecular Properties

- Molecules with one or more unpaired electrons are attracted into a magnetic field. The more unpaired electrons, the stronger the force of the attraction
- **Paramagnetism**: property that a substance possesses if it contains one or more unpaired electrons. A paramagnetic substance is drawn into a magnetic field
- **Diamagnetism**: type of magnetism that causes a substance with no unpaired electrons to be weakly repelled from a magnetic field.
- Diamagnetism is a much weaker effect than paramagnetism
- As bond orders increase, bond distances decrease and bond-dissociation energies increase.
- Molecules with the same bond order do not have the same bond distances and bond-dissociation energies. There are other factors involved, such as nuclear charges and the extend of orbital overlap.

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10: GASES

Previously, we focused on the *microscopic* properties of matter—the properties of individual atoms, ions, and molecules—and how the electronic structures of atoms and ions determine the stoichiometry and three-dimensional geometry of the compounds they form. We will now focus on *macroscopic* properties—the behavior of aggregates with large numbers of atoms, ions, or molecules. An understanding of macroscopic properties is central to an understanding of chemistry. Why, for example, are many substances gases under normal pressures and temperatures (1.0 atm, 25°C), whereas others are liquids or solids? We will examine each form of matter—gases, liquids, and solids—as well as the nature of the forces, such as hydrogen bonding and electrostatic interactions, that hold molecular and ionic compounds together in these three states.

In this chapter, we explore the relationships among pressure, temperature, volume, and the amount of gases. You will learn how to use these relationships to describe the physical behavior of a sample of both a pure gaseous substance and mixtures of gases. By the end of this chapter, your understanding of the gas laws and the model used to explain the behavior of gases will allow you to explain how straws and hot-air balloons work, why hand pumps cannot be used in wells beyond a certain depth, why helium-filled balloons deflate so rapidly, and how a gas can be liquefied for use in preserving biological tissue.

10.1: Characteristics of Gases

10.2: Pressure

10.3: The Gas Laws

10.4: The Ideal Gas Equation

10.5: Further Applications of the Ideal-Gas Equations

10.6: Gas Mixtures and Partial Pressures

10.7: Kinetic-Molecular Theory

10.8: Molecular Effusion and Diffusion

10.9: Real Gases - Deviations from Ideal Behavior

10.E: Exercises

10.S: Gases (Summary)

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10.1: Characteristics of Gases

Learning Objectives

- To describe the characteristics of a gas.

The three common phases (or states) of matter are gases, liquids, and solids. Gases have the lowest density of the three, are highly compressible, and completely fill any container in which they are placed. Gases behave this way because their intermolecular forces are relatively weak, so their molecules are constantly moving independently of the other molecules present. Solids, in contrast, are relatively dense, rigid, and incompressible because their intermolecular forces are so strong that the molecules are essentially locked in place. Liquids are relatively dense and incompressible, like solids, but they flow readily to adapt to the shape of their containers, like gases. We can therefore conclude that the sum of the intermolecular forces in liquids are between those of gases and solids. Figure 10.1.1 compares the three states of matter and illustrates the differences at the molecular level.

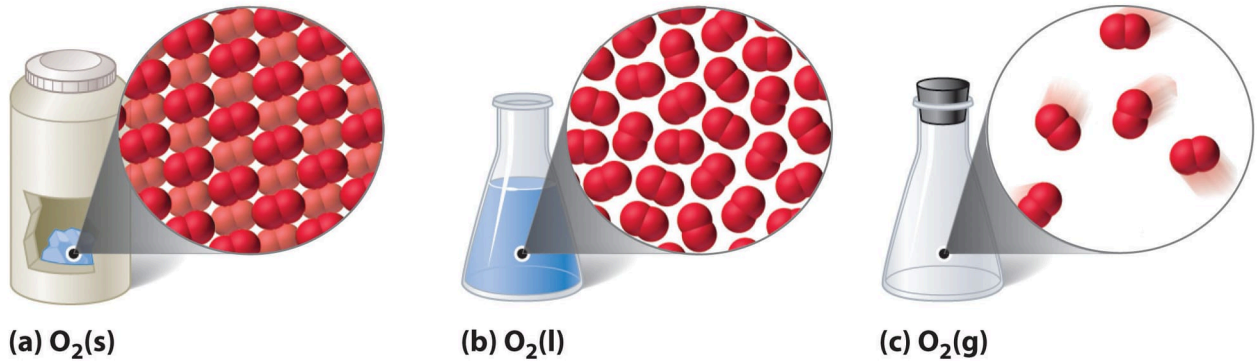


Figure 10.1.1: A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States: (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

The state of a given substance depends strongly on conditions. For example, H_2O is commonly found in all three states: solid ice, liquid water, and water vapor (its gaseous form). Under most conditions, we encounter water as the liquid that is essential for life; we drink it, cook with it, and bathe in it. When the temperature is cold enough to transform the liquid to ice, we can ski or skate on it, pack it into a snowball or snow cone, and even build dwellings with it. Water vapor (the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions so nitrogen (N_2) and oxygen (O_2) are referred to as gases, but gaseous water in the atmosphere is called water vapor) is a component of the air we breathe, and it is produced whenever we heat water for cooking food or making coffee or tea. Water vapor at temperatures greater than 100°C is called steam. Steam is used to drive large machinery, including turbines that generate electricity. The properties of the three states of water are summarized in Table 10.1.

Table 10.1.1: Properties of Water at 1.0 atm

Temperature	State	Density (g/cm3)
≤0°C	solid (ice)	0.9167 (at 0.0°C)
0°C–100°C	liquid (water)	0.9997 (at 4.0°C)
≥100°C	vapor (steam)	0.005476 (at 127°C)

The geometric structure and the physical and chemical properties of atoms, ions, and molecules usually do *not* depend on their physical state; the individual water molecules in ice, liquid water, and steam, for example, are all identical. In contrast, the

macroscopic properties of a substance depend strongly on its physical state, which is determined by intermolecular forces and conditions such as temperature and pressure.

Figure 10.1.2 shows the locations in the periodic table of those elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble gases (group 18) are monatomic gases, whereas the other gaseous elements are diatomic molecules (**H_2, N_2, O_2, F_2, and Cl_2**). Oxygen can also form a second allotrope, the highly reactive triatomic molecule ozone (**O_3**), which is also a gas. In contrast, bromine (as Br_2) and mercury (Hg) are liquids under normal conditions (25°C and 1.0 atm, commonly referred to as "room temperature and pressure"). Gallium (Ga), which melts at only 29.76°C, can be converted to a liquid simply by holding a container of it in your hand or keeping it in a non-air-conditioned room on a hot summer day. The rest of the elements are all solids under normal conditions.

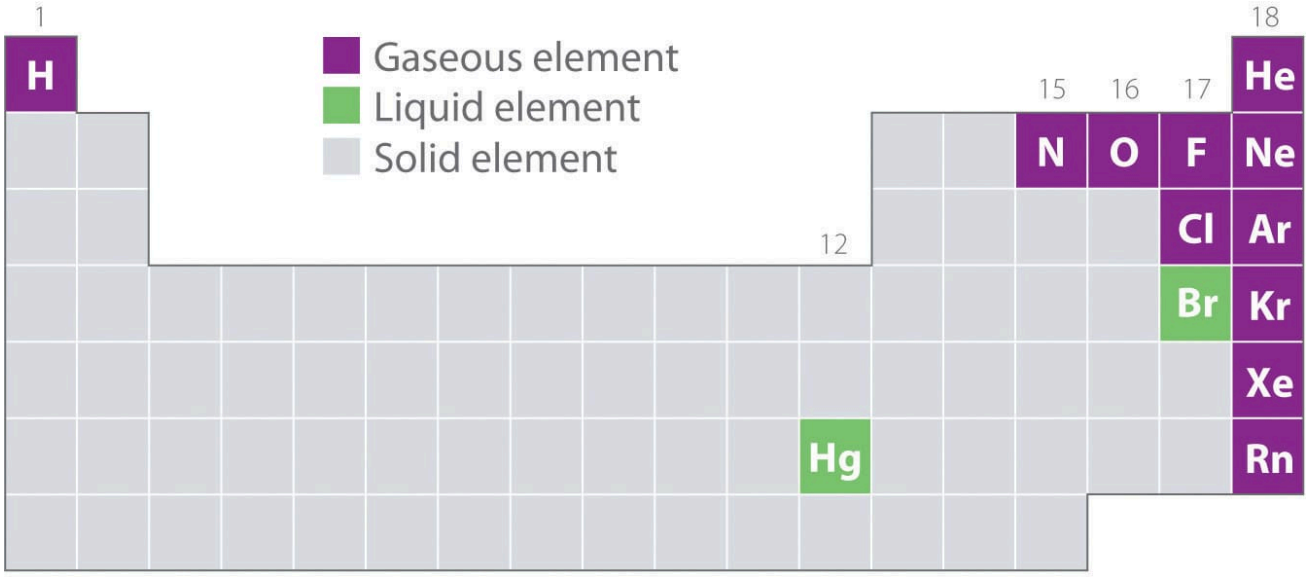


Figure 10.1.2: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

Purple elements are gaseous elements, green are liquid, and gray and solid. H, N, O, F, Cl, He, Ne, Ar, Kr, Xe, and Rn are all purple. Br and Hg are green. The rest are gray.

All of the gaseous elements (other than the monatomic noble gases) are molecules. Within the same group (1, 15, 16 and 17), the lightest elements are gases. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms.

Summary

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2, O_2).

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10.2: Pressure

Learning Objectives

- to describe and measure the pressure of a gas.

At the macroscopic level, a complete physical description of a sample of a gas requires four quantities:

- ***temperature*** (expressed in kelvins),
- ***volume*** (expressed in liters),
- ***amount*** (expressed in moles), and
- ***pressure*** (in atmospheres).

As we demonstrated below, these variables are *not* independent (i.e., they cannot be arbitrarily be varied). If we know the values of any *three* of these quantities, we can calculate the fourth and thereby obtain a full physical description of the gas. Temperature, volume, and amount have been discussed in previous chapters. We now discuss pressure and its units of measurement.

Units of Pressure

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. The air in a balloon, for example, exerts a force against the interior surface of the balloon, and a liquid injected into a mold exerts a force against the interior surface of the mold, just as a chair exerts a force against the floor because of its mass and the effects of gravity. If the air in a balloon is heated, the increased kinetic energy of the gas eventually causes the balloon to burst because of the increased pressure (P) of the gas, the force (F) per unit area (A) of surface:

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \tag{10.2.1}$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 10.2.1 that applying the same force to a smaller area produces a higher pressure. When we use a hose to wash a car, for example, we can increase the pressure of the water by reducing the size of the opening of the hose with a thumb.

The units of pressure are derived from the units used to measure force and area. The SI unit for pressure, derived from the SI units for force (newtons) and area (square meters), is the newton per square meter (N/m^2), which is called the **Pascal (Pa)**, after the French mathematician Blaise Pascal (1623–1662):

$$1\ \text{Pa} = 1\ \text{N/m}^2 \tag{10.2.2}$$

Example 10.2.1

Assuming a paperback book has a mass of 2.00 kg, a length of 27.0 cm, a width of 21.0 cm, and a thickness of 4.5 cm, what pressure does it exert on a surface if it is

a. lying flat?
b. standing on edge in a bookcase?

Given: mass and dimensions of object

Asked for: pressure

Strategy:

A. Calculate the force exerted by the book and then compute the area that is in contact with a surface.

B. Substitute these two values into Equation 10.2.1 to find the pressure exerted on the surface in each orientation.

Solution:

The force exerted by the book does *not* depend on its orientation. Recall that the force exerted by an object is $F = ma$, where m is its mass and a is its acceleration. In Earth's gravitational field, the acceleration is due to gravity (9.8067 m/s^2 at Earth's surface). In SI units, the force exerted by the book is therefore

$$F = ma = 2.00\ \text{kg} \times 9.8067\frac{\text{m}}{\text{s}^2} = 19.6\frac{\text{kg} \cdot \text{m}}{\text{s}^2} = 19.6\ \text{N}$$

A We calculated the force as 19.6 N. When the book is lying flat, the area is

$$A = 0.270\ \text{m} \times 0.210\ \text{m} = 0.0567\ \text{m}^2.$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{F}{A} = \frac{19.6\ \text{N}}{0.0567\ \text{m}^2} = 3.46 \times 10^2 \text{Pa}$$

A If the book is standing on its end, the force remains the same, but the area decreases:

$$\text{A} = 21.0\ \text{cm} \times 4.5\ \text{cm} = 0.210\ \text{m} \times 0.045\ \text{m} = 9.5 \times 10^{-3}\ \text{m}^2$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{19.6\ \text{N}}{9.5 \times 10^{-3}\ \text{m}^2} = 2.06 \times 10^3\ \text{Pa}$$

Exercise 10.2.1

What pressure does a 60.0 kg student exert on the floor

a. when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?
b. as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answer a available at the end of this section.

Barometric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface (Figure 10.2.1). Every point on Earth's surface experiences a net pressure called ***barometric pressure***. The pressure exerted by the atmosphere is considerable: a 1 m^2 column, measured from sea level to the top of the atmosphere, has a mass of about 10,000 kg, which gives a pressure of about 101 kPa:

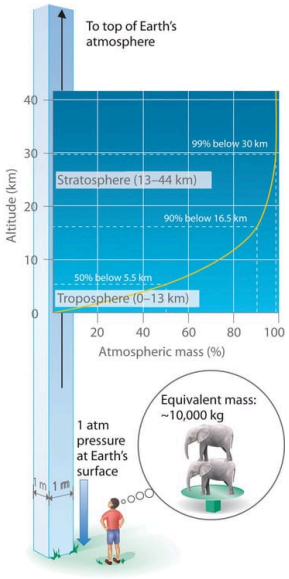


Figure 10.2.1: Barometric Pressure. Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface.

Barometric pressure can be measured using a barometer, a device invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). A barometer may be constructed from a long glass tube that is closed at one end. It is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside (Figure 10.2.2). Why doesn't all the mercury run out? Gravity is certainly exerting a downward force on the mercury in the tube, but it is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a vacuum), there is no pressure pushing down on the column. Thus the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere. The pressure exerted by the mercury column can be expressed as:

$$P = \frac{F}{A} \tag{10.2.3}$$

$$= \frac{mg}{A} \tag{10.2.4}$$

$$= \frac{\rho V \cdot g}{A} \tag{10.2.5}$$

$$= \frac{\rho \cdot Ah \cdot g}{A} \tag{10.2.6}$$

$$= \rho g h \tag{10.2.7}$$

with

- g is the gravitational acceleration,
- m is the mass,
- ρ is the density,
- V is the volume,
- A is the bottom area, and
- h is height of the mercury column.

Under normal weather conditions at sea level, the two forces are balanced when the top of the mercury column is approximately 760 mm above the level of the mercury in the dish, as shown in Figure 10.2.2. This value varies with meteorological conditions and altitude. In Denver, Colorado, for example, at an elevation of about 1 mile, or 1609 m (5280 ft), the height of the mercury column is 630 mm rather than 760 mm.

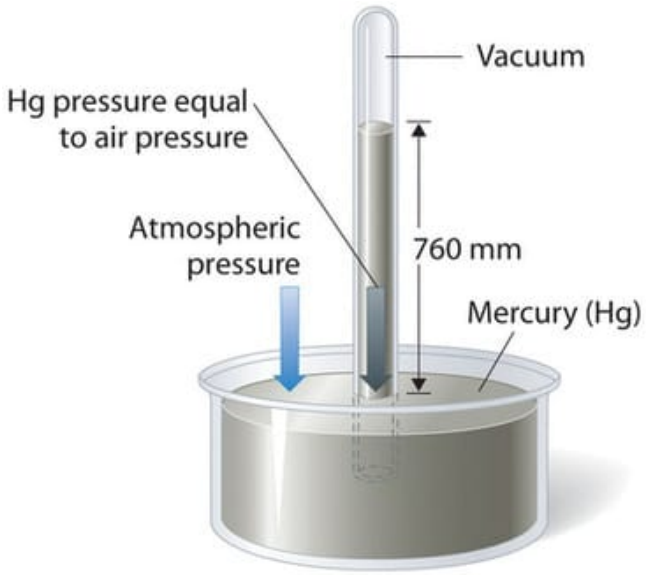


Figure 10.2.2: A Mercury Barometer. The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the mercury column.

Mercury barometers have been used to measure barometric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg), often called the torr, after Torricelli. Standard barometric pressure is the barometric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm). These units are also related to the pascal:

$$1 \text{ atm} = 760\ mmHg \tag{10.2.8}$$
$$= 760\ torr \tag{10.2.9}$$
$$= 1.01325 \times 10^5\ Pa \tag{10.2.10}$$
$$= 101.325\ kPa \tag{10.2.11}$$

Thus a pressure of 1 atm equals 760 mmHg exactly.

We are so accustomed to living under this pressure that we never notice it. Instead, what we notice are *changes* in the pressure, such as when our ears pop in fast elevators in skyscrapers or in airplanes during rapid changes in altitude. We make use of barometric pressure in many ways. We can use a drinking straw because sucking on it removes air and thereby reduces the pressure inside the straw. The barometric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

Example 10.2.2: Barometric Pressure

One of the authors visited Rocky Mountain National Park several years ago. After departing from an airport at sea level in the eastern United States, he arrived in Denver (altitude 5280 ft), rented a car, and drove to the top of the highway outside Estes Park (elevation 14,000 ft). He noticed that even slight exertion was very difficult at this altitude, where the barometric pressure is only 454 mmHg. Convert this pressure to

a. atmospheres (atm).
b. bar.

Given: pressure in millimeters of mercury

Asked for: pressure in atmospheres and bar

Strategy:

Use the conversion factors in Equation 10.2.11 to convert from millimeters of mercury to atmospheres and kilopascals.

Solution:

From Equation 10.2.11, we have 1 atm = 760 mmHg = 101.325 kPa. The pressure at 14,000 ft in atm is thus

$$P = 454 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \tag{10.2.12}$$
$$= 0.597 \ atm$$

The pressure in bar is given by

$$P = 0.597 \text{ atm} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} \tag{10.2.13}$$
$$= 0.605 \ bar$$

Exercise 10.2.2: Barometric Pressure

Mt. Everest, at 29,028 ft above sea level, is the world's tallest mountain. The normal barometric pressure at this altitude is about 0.308 atm. Convert this pressure to

a. millimeters of mercury.
b. bar.

Answer a available at the end of this section.

Manometers

Barometers measure barometric pressure, but manometers measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in part (a) in Figure 10.2.3. When the bulb contains no gas (i.e., when its interior is a near vacuum), the heights of the two columns of mercury are the same because the space above the mercury on the left is a near vacuum (it contains only traces of mercury vapor). If a gas is released into the bulb on the right, it will exert a pressure on the mercury in the right column, and the two columns of mercury will no longer be the same height. The *difference* between the heights of the two columns is equal to the pressure of the gas.

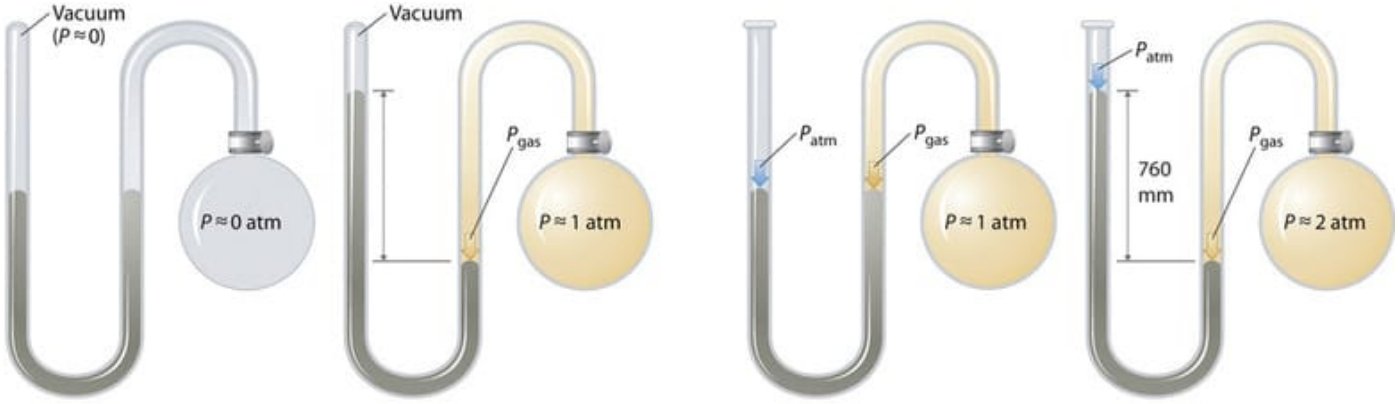


Figure 10.2.3: The Two Types of Manometer. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere ($P \approx 1$ atm), and the difference in the heights of the two columns gives the *difference* between barometric pressure and the pressure of the gas in the bulb.

If the tube is open to the atmosphere instead of closed, as in the open-end manometer shown in part (b) in Figure 10.2.3, then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the barometric pressure. If the gas in the bulb has a *higher* pressure, the mercury in the open tube will be forced up by the gas pushing down on the mercury

in the other arm of the U-shaped tube. The pressure of the gas in the bulb is therefore the sum of the barometric pressure (measured with a barometer) and the difference in the heights of the two columns. If the gas in the bulb has a pressure *less* than that of the atmosphere, then the height of the mercury will be greater in the arm attached to the bulb. In this case, the pressure of the gas in the bulb is the barometric pressure minus the difference in the heights of the two columns.

Example 10.2.3

Suppose you want to construct a closed-end manometer to measure gas pressures in the range 0.000–0.200 atm. Because of the toxicity of mercury, you decide to use water rather than mercury. How tall a column of water do you need? (The density of water is 1.00 g/cm^3; the density of mercury is 13.53 g/cm^3.)

Given: pressure range and densities of water and mercury

Asked for: column height

Strategy:

A. Calculate the height of a column of mercury corresponding to 0.200 atm in millimeters of mercury. This is the height needed for a mercury-filled column.
B. From the given densities, use a proportion to compute the height needed for a water-filled column.

Solution:

A In millimeters of mercury, a gas pressure of 0.200 atm is

$$P = 0.200 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 152 \text{ mmHg}$$

Using a mercury manometer, you would need a mercury column at least 152 mm high.

B Because water is less dense than mercury, you need a *taller* column of water to achieve the same pressure as a given column of mercury. The height needed for a water-filled column corresponding to a pressure of 0.200 atm is proportional to the ratio of the density of mercury to the density of water

$$P = d_{\text{wat}} g h_{\text{wat}} = d_{\text{Hg}} g h_{\text{Hg}}$$

$$h_{\text{wat}} = h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} = 152 \text{ mm} \times \frac{13.53 \text{ g/cm}^3}{1.00 \text{ g/cm}^3} = 2070 \text{ mm}$$

The answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

Exercise 10.2.3

Suppose you want to design a barometer to measure barometric pressure in an environment that is always hotter than 30°C. To avoid using mercury, you decide to use gallium, which melts at 29.76°C; the density of liquid gallium at 25°C is 6.114 g/cm^3. How tall a column of gallium do you need if P = 1.00 atm?

Answer available at the end of this section.

The answer to Example 10.2.3 also tells us the maximum depth of a farmer's well if a simple suction pump will be used to get the water out. The 1.00 atm corresponds to a column height of

$$
\begin{aligned}
h_{\text{wat}} &= h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} \\
&= 760 \text{ mm} \times \frac{13.53 \text{ g/cm}^3}{1.00 \text{ g/cm}^3} \\
&= 1.03 \times 10^4 \ mm \\
&= 10.3 \ m
\end{aligned}
$$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on barometric pressure to force the liquid up a tube. If 1 atm pressure corresponds to a 10.3 m (33.8 ft) column of water, then it is physically impossible for barometric pressure to raise the water in a well higher than this. Until electric pumps were invented to push water mechanically from greater depths, this factor greatly limited where people could live because obtaining water from wells deeper than about 33 ft was difficult.

Summary

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. Four quantities must be known for a complete physical description of a sample of a gas: *temperature*, *volume*, *amount*, and *pressure*. **Pressure** is force per unit area of surface; the SI unit for pressure is the **pascal (Pa)**, defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area on which the force is exerted. The pressure exerted by Earth's atmosphere, called *barometric pressure*, is about 101 kPa or 14.7 $lb/in.^2$ at sea level. barometric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to barometric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard barometric pressure**, the pressure required to support a column of mercury 760 mm tall, is yet another unit of pressure: 1 **atmosphere (atm)**. A **manometer** is an apparatus used to measure the pressure of a sample of a gas.

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Answers

Exercise 10.2.1

3.27 × 10^4 Pa

5.9 × 10^6 Pa

Exercise 10.2.2**: Barometric Pressure**

234 mmHg;

0.312 bar

Exercise 10.2.3

1.68 m

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10.3: The Gas Laws

Learning Objectives

- To understand the relationships among pressure, temperature, volume, and the amount of a gas.

Early scientists explored the relationships among the pressure of a gas (*P*) and its temperature (*T*), volume (*V*), and amount (*n*) by holding two of the four variables constant (amount and temperature, for example), varying a third (such as pressure), and measuring the effect of the change on the fourth (in this case, volume). The history of their discoveries provides several excellent examples of the scientific method.

The Relationship between Pressure and Volume: Boyle's Law

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

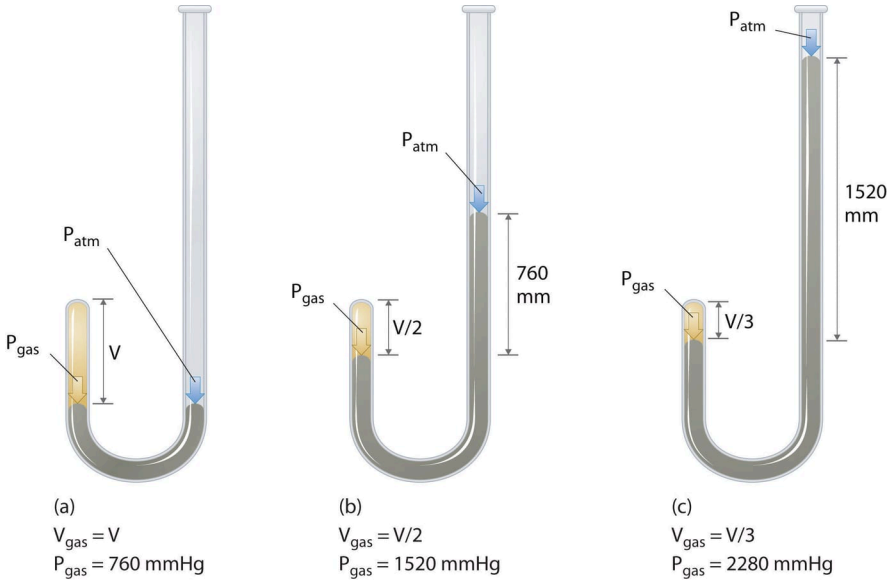


Figure 10.3.1: Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is *V*. (b) If enough mercury is added to the right side to give a difference in height of 760 mmHg between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is *V*/2. (c) If an additional 760 mmHg is added to the column on the right, the total pressure on the gas increases to 2280 mmHg, and the volume of the gas decreases to *V*/3 (CC BY-SA-NC; anonymous).

The Irish chemist Robert Boyle (1627–1691) carried out some of the earliest experiments that determined the quantitative relationship between the pressure and the volume of a gas. Boyle used a J-shaped tube partially filled with mercury, as shown in Figure 10.3.1. In these experiments, a small amount of a gas or air is trapped above the mercury column, and its volume is measured at atmospheric pressure and constant temperature. More mercury is then poured into the open arm to increase the pressure on the gas sample. The pressure on the gas is atmospheric pressure plus the difference in the heights of the mercury columns, and the resulting volume is measured. This process is repeated until either there is no more room in the open arm or the volume of the gas is too small to be measured accurately. Data such as those from one of Boyle's own experiments may be plotted in several ways (Figure 10.3.2). A simple plot of V versus P gives a curve called a hyperbola and reveals an inverse relationship between pressure and volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the

two quantities is described as follows:

$$PV = \text{constant} \tag{10.3.1}$$

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V:

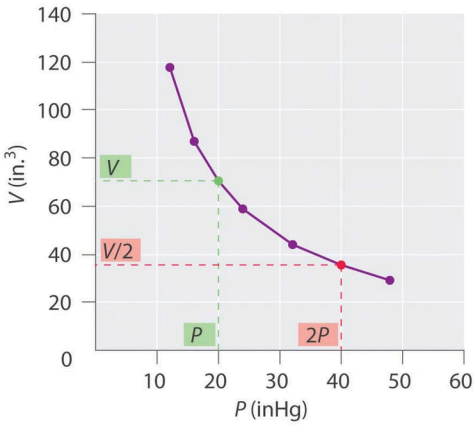
$$V = \frac{\text{const.}}{P} = \text{const.}\left(\frac{1}{P}\right) \tag{10.3.2}$$

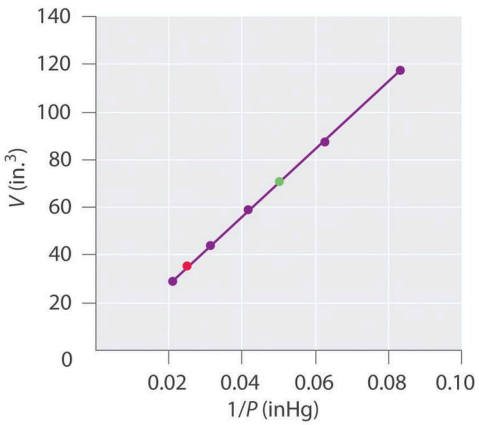
or

$$V \propto \frac{1}{P} \tag{10.3.3}$$

where the $\propto$ symbol is read "is proportional to." A plot of *V* versus 1/*P* is thus a straight line whose slope is equal to the constant in Equations 10.3.1 and 10.3.3. Dividing both sides of Equation 10.3.1 by *V* instead of *P* gives a similar relationship between *P* and 1/*V*. The numerical value of the constant depends on the amount of gas used in the experiment and on the temperature at which the experiments are carried out. This relationship between pressure and volume is known as Boyle's law, after its discoverer, and can be stated as follows: *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure*. This law in practice is shown in Figure 10.3.2.

P (inHg)	*V* (in.^{3})	*PV*
12.0	117.5	1410
16.0	87.2	1400
20.0	70.7	1410
24.0	58.8	1410
32.0	44.2	1410
40.0	35.3	1410
48.0	29.1	1400





(a) Data from Boyle's experiment **(b) Volume vs. pressure** **(c) Volume vs. 1/pressure**

Figure 10.3.2: Plots of Boyle's Data. (a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.^{3} rather than cm^3) and the pressure (in. Hg rather than mmHg). (b) This plot of pressure versus volume is a hyperbola. Because *PV* is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) A plot of volume versus 1/pressure for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation *V* = constant/*P* (CC BY-SA-NC; anonymous).

At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure

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The Relationship between Temperature and Volume: Charles's Law

Hot air rises, which is why hot-air balloons ascend through the atmosphere and why warm air collects near the ceiling and cooler air collects at ground level. Because of this behavior, heating registers are placed on or near the floor, and vents for air-conditioning are placed on or near the ceiling. The fundamental reason for this behavior is that gases expand when they are

heated. Because the same amount of substance now occupies a greater volume, hot air is less dense than cold air. The substance with the lower density—in this case hot air—rises through the substance with the higher density, the cooler air.

The first experiments to quantify the relationship between the temperature and the volume of a gas were carried out in 1783 by an avid balloonist, the French chemist Jacques Alexandre César Charles (1746–1823). Charles's initial experiments showed that a plot of the volume of a given sample of gas versus temperature (in degrees Celsius) at constant pressure is a straight line. Similar but more precise studies were carried out by another balloon enthusiast, the Frenchman Joseph-Louis Gay-Lussac (1778–1850), who showed that a plot of V versus T was a straight line that could be extrapolated to a point at zero volume, a theoretical condition now known to correspond to –273.15°C (Figure 10.3.3).A sample of gas cannot really have a volume of zero because any sample of matter must have some volume. Furthermore, at 1 atm pressure all gases liquefy at temperatures well above –273.15°C. Note from part (a) in Figure 10.3.3 that the slope of the plot of V versus T varies for the same gas at different pressures but that the intercept remains constant at –273.15°C. Similarly, as shown in part (b) in Figure 10.3.3, plots of V versus T for different amounts of varied gases are straight lines with different slopes but the same intercept on the T axis.

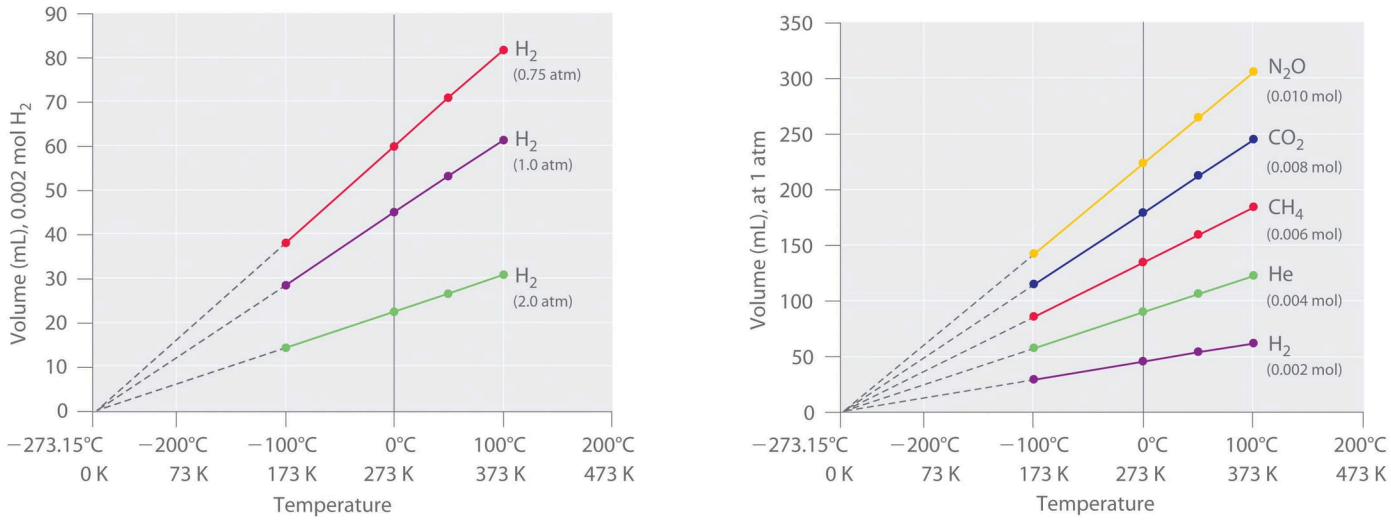


Figure 10.3.3: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to –100°C, and the broken lines show the extrapolation of the data to $V = 0$. The temperature scale is given in both degrees Celsius and kelvins. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at $V = 0$ (–273.15°C = 0 K). (b) In these plots of volume versus temperature for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of $V = 0$ at –273.15°C, regardless of the identity or the amount of the gas (CC BY-SA-NC; anonymous).

The significance of the invariant T intercept in plots of V versus T was recognized in 1848 by the British physicist William Thomson (1824–1907), later named Lord Kelvin. He postulated that –273.15°C was the lowest possible temperature that could theoretically be achieved, for which he coined the term absolute zero (0 K).

We can state Charles's and Gay-Lussac's findings in simple terms: At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in kelvins). This relationship, illustrated in part (b) in Figure 10.3.3 is often referred to as Charles's law and is stated mathematically as

$$V = \text{const. } T \tag{10.3.4}$$

or

$$V \propto T \tag{10.3.5}$$

with *temperature expressed in kelvins,* not *in degrees Celsius.* Charles's law is valid for virtually all gases at temperatures well above their boiling points.

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The Relationship between Amount and Volume: Avogadro's Law

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac's work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles (Figure 10.3.4). This is the historic "Avogadro's hypothesis."

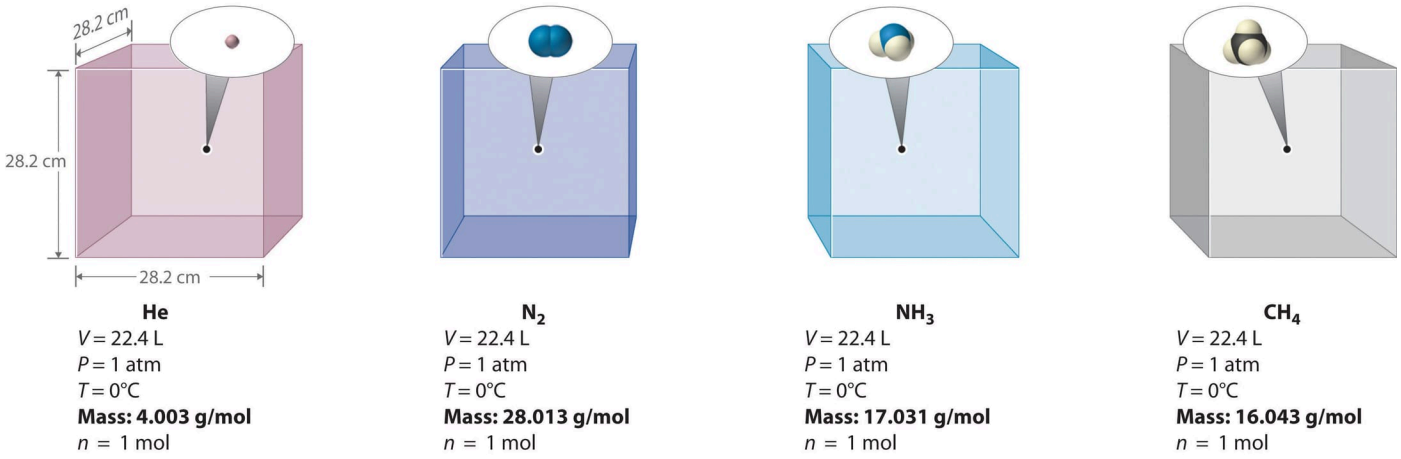


Figure 10.3.4: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous).

A logical corollary to Avogadro's hypothesis (sometimes called Avogadro's law) describes the relationship between the volume and the amount of a gas: *At constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.* Stated mathematically,

$$V = \text{const.}\ (n) \tag{10.3.6}$$

or

$$V \propto .n@\ \text{constant T and P} \tag{10.3.7}$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.

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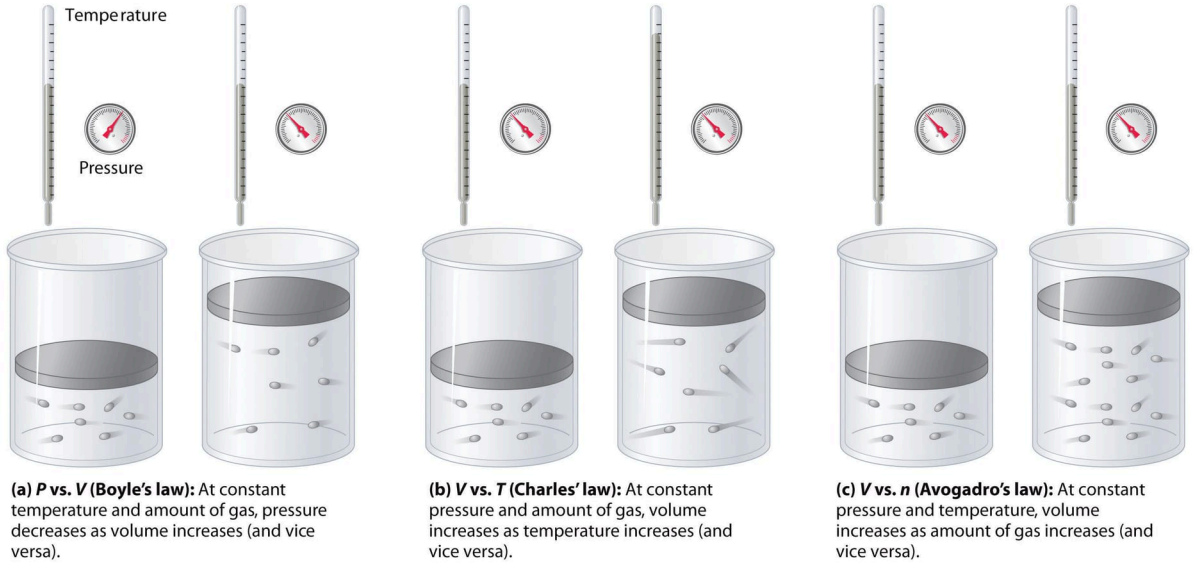
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For a sample of gas,

- *V* increases as *P* decreases (and vice versa)
- *V* increases as *T* increases (and vice versa)
- *V* increases as *n* increases (and vice versa)

The relationships among the volume of a gas and its pressure, temperature, and amount are summarized in Figure 10.3.5. Volume *increases* with increasing temperature or amount, but *decreases* with increasing pressure.



(a) *P* vs. *V* (Boyle's law): At constant temperature and amount of gas, pressure decreases as volume increases (and vice versa).

(b) *V* vs. *T* (Charles' law): At constant pressure and amount of gas, volume increases as temperature increases (and vice versa).

(c) *V* vs. *n* (Avogadro's law): At constant pressure and temperature, volume increases as amount of gas increases (and vice versa).

Figure 10.3.5: The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas. The thermometer and pressure gauge indicate the temperature and the pressure qualitatively, the level in the flask indicates the volume, and the number of particles in each flask indicates relative amounts (CC BY-SA-NC; anonymous).

Summary

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to its pressure (**Boyle's law**), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature (in kelvins) at constant pressure (**Charles's law**), and Avogadro postulated that the volume of a gas is directly proportional to the number of moles of gas present (**Avogadro's law**). Plots of the volume of gases versus temperature extrapolate to zero volume at –273.15°C, which is **absolute zero (0 K)**, the lowest temperature possible. Charles's law implies that the volume of a gas is directly proportional to its absolute temperature.

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10.4: The Ideal Gas Equation

Learning Objectives

- Derive the ideal gas law from the constituent gas laws
- To use the ideal gas law to describe the behavior of a gas.

In this module, the relationship between pressure, temperature, volume, and amount of a gas are described and how these relationships can be combined to give a general expression that describes the behavior of a gas.

Deriving the Ideal Gas Law

Any set of relationships between a single quantity (such as V) and several other variables (P, T, and n) can be combined into a single expression that describes all the relationships simultaneously. The three individual expressions were derived previously:

- **Boyle's law**

$$V \propto \frac{1}{P} \quad @ \text{ constant n and T}$$

- **Charles's law**

$$V \propto T \quad @ \text{ constant n and P}$$

- **Avogadro's law**

$$V \propto n \quad @ \text{ constant T and P}$$

Combining these three expressions gives

$$V \propto \frac{nT}{P} \tag{10.4.1}$$

which shows that the volume of a gas is proportional to the number of moles and the temperature and inversely proportional to the pressure. This expression can also be written as

$$V = \text{Cons.} \left(\frac{nT}{P}\right) \tag{10.4.2}$$

By convention, the proportionality constant in Equation 10.4.1 is called the gas constant, which is represented by the letter R. Inserting R into Equation 10.4.2 gives

$$V = \frac{RnT}{P} = \frac{nRT}{P} \tag{10.4.3}$$

Clearing the fractions by multiplying both sides of Equation 10.4.4 by P gives

$$PV = nRT \tag{10.4.4}$$

This equation is known as the **ideal gas law**.

An ideal gas is defined as a hypothetical gaseous substance whose behavior is independent of attractive and repulsive forces and can be completely described by the ideal gas law. In reality, there is no such thing as an ideal gas, but an ideal gas is a useful conceptual model that allows us to understand how gases respond to changing conditions. As we shall see, under many conditions, most real gases exhibit behavior that closely approximates that of an ideal gas. The ideal gas law can therefore be used to predict the behavior of real gases under most conditions. The ideal gas law does not work well at very low temperatures or very high pressures, where deviations from ideal behavior are most commonly observed.

Significant deviations from ideal gas behavior commonly occur at low temperatures and very high pressures.

Before we can use the ideal gas law, however, we need to know the value of the gas constant R. Its form depends on the units used for the other quantities in the expression. If V is expressed in liters (L), P in atmospheres (atm), T in kelvins (K), and n in moles (mol), then

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \tag{10.4.5}$$

Because the product PV has the units of energy, R can also have units of J/(K•mol):

$$R = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \tag{10.4.6}$$

Standard Conditions of Temperature and Pressure

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and $1 \text{ bar} = 100 \text{ kPa} = 10^5 \text{ Pa}$ pressure, referred to as standard temperature and pressure (**STP**).

$$\text{STP:} \qquad T = 273.15 \text{ K and } P = 1 \text{ bar} = 10^5 \text{ Pa}$$

Please note that STP was defined differently in the past. The old definition was based on a standard pressure of 1 atm.

We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the ideal gas law given in Equation 10.4.4:

$$V = \frac{nRT}{P} \tag{10.4.7}$$

Thus the volume of 1 mol of an ideal gas is **22.71 L at STP** and **22.41 L at 0°C and 1 atm**, approximately equivalent to the volume of three basketballs. The molar volumes of several real gases at 0°C and 1 atm are given in Table 10.3, which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at 0°C and 1 atm. The relationships described in Section 10.3 as Boyle's, Charles's, and Avogadro's laws are simply special cases of the ideal gas law in which two of the four parameters (P, V, T, and n) are held fixed.

Table 10.4.1: Molar Volumes of Selected Gases at 0°C and 1 atm

Gas	Molar Volume (L)
He	22.434
Ar	22.397
H_2	22.433
N_2	22.402
O_2	22.397
CO_2	22.260
NH_3	22.079

Applying the Ideal Gas Law

The ideal gas law allows us to calculate the value of the fourth variable for a gaseous sample if we know the values of any three of the four variables (*P*, *V*, *T*, and *n*). It also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (*P*, *V*, *T*, and *n*) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same equation—the ideal gas law—and then determine which quantities are given and which need to be calculated. Let's begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

Example 10.4.1

The balloon that Charles used for his initial flight in 1783 was destroyed, but we can estimate that its volume was 31,150 L (1100 ft^3), given the dimensions recorded at the time. If the temperature at ground level was 86°F (30°C) and the atmospheric pressure was 745 mmHg, how many moles of hydrogen gas were needed to fill the balloon?

Given: volume, temperature, and pressure

Asked for: amount of gas

Strategy:

A. Solve the ideal gas law for the unknown quantity, in this case *n*.
B. Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

Solution:

A We are given values for *P*, *T*, and *V* and asked to calculate *n*. If we solve the ideal gas law (Equation 10.4.4) for n, we obtain

$$745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.980 \text{ atm}$$

B *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.08206 (L•atm)/(K•mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$T = 273 + 30 = 303\text{K}$$

Substituting these values into the expression we derived for *n*, we obtain

$$\begin{aligned} n &= \frac{PV}{RT} \\ &= \frac{0.980 \text{ atm} \times 31150 \text{ L}}{0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 303 \text{ K}} \\ &= 1.23 \times 10^3 \; mol \end{aligned}$$

Exercise 10.4.1

Suppose that an “empty” aerosol spray-paint can has a volume of 0.406 L and contains 0.025 mol of a propellant gas such as CO_2. What is the pressure of the gas at 25°C?

Answer available at the end of this section.

In Example 10.4.1, we were given three of the four parameters needed to describe a gas under a particular set of conditions, and we were asked to calculate the fourth. We can also use the ideal gas law to calculate the effect of *changes* in any of the specified conditions on any of the other parameters, as shown in Example 10.4.5.

General Gas Equation

When a gas is described under two different conditions, the ideal gas equation must be applied twice - to an initial condition and a final condition. This is:

$$\begin{array}{ll} \text{Initial condition } (i) & \text{Final condition}(f) \\ P_iV_i = n_iRT_i & P_fV_f = n_fRT_f \end{array}$$

Both equations can be rearranged to give:

$$R = \frac{P_i V_i}{n_i T_i} \qquad R = \frac{P_f V_f}{n_f T_f}$$

The two equations are equal to each other since each is equal to the same constant R. Therefore, we have:

$$\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f} \tag{10.4.8}$$

The equation is called the **general gas equation**. The equation is particularly useful when one or two of the gas properties are held constant between the two conditions. In such cases, the equation can be simplified by eliminating these constant gas properties.

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Example 10.4.2

Suppose that Charles had changed his plans and carried out his initial flight not in August but on a cold day in January, when the temperature at ground level was –10°C (14°F). How large a balloon would he have needed to contain the same amount of hydrogen gas at the same pressure as in Example 10.4.1?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A. Use the results from Example 10.4.1 for August as the initial conditions and then calculate the *change in volume* due to the change in temperature from 30°C to –10°C. Begin by constructing a table showing the initial and final conditions.
B. Simplify the general gas equation by eliminating the quantities that are held constant between the initial and final conditions, in this case P and n.
C. Solve for the unknown parameter.

Solution:

A To see exactly which parameters have changed and which are constant, prepare a table of the initial and final conditions:

Solution to Example 10.4.2

Initial (August)	Final (January)
$T_i = 30\ °C = 303\ K$	$T_f = -10\ °C = 263\ K$
$P_i = 0.980\ atm$	$P_f = 0.980\ atm$
$n_i = 1.23 \times 10^3\ mol$	$n_f = 1.23 \times 10^3\ mol$
$V_i = 31150\ L$	$V_f = ?$

B Both n and P are the same in both cases ($n_i = n_f, P_i = P_f$). Therefore, Equation 10.4.8 can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$\begin{aligned} V_f &= V_i \times \frac{T_f}{T_i} \\ &= 31150\ \text{L} \times \frac{263\ \text{K}}{303\ \text{K}} \\ &= 2.70 \times 10^4\ L \end{aligned}$$

It is important to check your answer to be sure that it makes sense, just in case you have accidentally inverted a quantity or multiplied rather than divided. In this case, the temperature of the gas decreases. Because we know that gas volume decreases with decreasing temperature, the final volume must be less than the initial volume, so the answer makes sense. We could have calculated the new volume by plugging all the given numbers into the ideal gas law, but it is generally much easier and faster to focus on only the quantities that change.

Exercise 10.4.2

At a laboratory party, a helium-filled balloon with a volume of 2.00 L at 22°C is dropped into a large container of liquid nitrogen (T = –196°C). What is the final volume of the gas in the balloon?

Answer available at the end of this section.

Example 10.4.1 illustrates the relationship originally observed by Charles. We could work through similar examples illustrating the inverse relationship between pressure and volume noted by Boyle (*PV* = constant) and the relationship between volume and amount observed by Avogadro (*V*/*n* = constant). We will not do so, however, because it is more important to note that the historically important gas laws are only special cases of the ideal gas law in which two quantities are varied while the other two remain fixed. The method used in Example 10.4.1 can be applied in *any* such case, as we demonstrate in Example 10.4.2 (which also shows why heating a closed container of a gas, such as a butane lighter cartridge or an aerosol can, may cause an explosion).

Example 10.4.3

Aerosol cans are prominently labeled with a warning such as “Do not incinerate this container when empty.” Assume that you did not notice this warning and tossed the “empty” aerosol can in Exercise 10.4.1 (0.025 mol in 0.406 L, initially at 25°C and 1.5 atm internal pressure) into a fire at 750°C. What would be the pressure inside the can (if it did not explode)?

Given: initial volume, amount, temperature, and pressure; final temperature

Asked for: final pressure

Strategy:

Follow the strategy outlined in Example 10.4.2.

Solution:

Prepare a table to determine which parameters change and which are held constant:

Solution to Example 10.4.3

Initial	Final
$V_i = 0.406\ \text{L}$	$V_f = 0.406\ \text{L}$

Initial	Final
$n_i = 0.025\ \text{mol}$	$n_f = 0.025\ \text{mol}$
$T_i = 25\ ^\circ\text{C} = 298\ \text{K}$	$T_i = 750\ ^\circ\text{C} = 1023\ \text{K}$
$P_i = 1.5\ \text{atm}$	$P_f = ?$

Both V and n are the same in both cases ($V_i = V_f, n_i = n_f$). Therefore, Equation can be simplified to:

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

By solving the equation for P_f, we get:

$$\begin{aligned} P_f &= P_i \times \frac{T_f}{T_i} \\ &= 1.5\ \text{atm} \times \frac{1023\ \text{K}}{298\ \text{K}} \\ &= 5.1\ atm \end{aligned}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

Exercise 10.4.3

Suppose that a fire extinguisher, filled with CO_2 to a pressure of 20.0 atm at 21°C at the factory, is accidentally left in the sun in a closed automobile in Tucson, Arizona, in July. The interior temperature of the car rises to 160°F (71.1°C). What is the internal pressure in the fire extinguisher?

Answer available at the end of this section.

In Examples 10.4.1 and 10.4.2, two of the four parameters (*P*, *V*, *T*, and *n*) were fixed while one was allowed to vary, and we were interested in the effect on the value of the fourth. In fact, we often encounter cases where two of the variables *P*, *V*, and *T* are allowed to vary for a given sample of gas (hence *n* is constant), and we are interested in the change in the value of the third under the new conditions.

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Example 10.4.4

We saw in Example 10.4.1 that Charles used a balloon with a volume of 31,150 L for his initial ascent and that the balloon contained 1.23×10^3 mol of H_2 gas initially at 30°C and 745 mmHg. Suppose that Gay-Lussac had also used this balloon for his record-breaking ascent to 23,000 ft and that the pressure and temperature at that altitude were 312 mmHg and –30°C, respectively. To what volume would the balloon have had to expand to hold the same amount of hydrogen gas at the higher altitude?

Given: initial pressure, temperature, amount, and volume; final pressure and temperature

Asked for: final volume

Strategy:

Follow the strategy outlined in Example 10.4.3.

Solution:

Begin by setting up a table of the two sets of conditions:

Solution to Example 10.4.4

Initial	Final
$P_i = 745\ \text{mmHg} = 0.980\ \text{atm}$	$P_f = 312\ \text{mmHg} = 0.411\ \text{atm}$
$T_i = 30\ ^\circ\text{C} = 303\ \text{K}$	$T_f = 750 - 30\ ^\circ\text{C} = 243\ \text{K}$
$n_i = 1.2 \times 10^3\ \text{mol}$	$n_i = 1.2 \times 10^3\ \text{mol}$
$V_i = 31150\ \text{L}$	$V_f = ?$

By eliminating the constant property (n) of the gas, Equation 10.4.8 is simplified to:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

By solving the equation for V_f, we get:

$$\begin{aligned} V_f &= V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i} \\ &= 3.115 \times 10^4\ \text{L} \times \frac{0.980\ \text{atm}}{0.411\ \text{atm}}\frac{243\ \text{K}}{303\ \text{K}} \\ &= 5.96 \times 10^4\ L \end{aligned}$$

Does this answer make sense? Two opposing factors are at work in this problem: decreasing the pressure tends to *increase* the volume of the gas, while decreasing the temperature tends to *decrease* the volume of the gas. Which do we expect to predominate? The pressure drops by more than a factor of two, while the absolute temperature drops by only about 20%. Because the volume of a gas sample is directly proportional to both *T* and 1/*P*, the variable that changes the most will have the greatest effect on *V*. In this case, the effect of decreasing pressure predominates, and we expect the volume of the gas to increase, as we found in our calculation.

We could also have solved this problem by solving the ideal gas law for *V* and then substituting the relevant parameters for an altitude of 23,000 ft:

Except for a difference caused by rounding to the last significant figure, this is the same result we obtained previously. *There is often more than one "right" way to solve chemical problems.*

Exercise 10.4.4

A steel cylinder of compressed argon with a volume of 0.400 L was filled to a pressure of 145 atm at 10°C. At 1.00 atm pressure and 25°C, how many 15.0 mL incandescent light bulbs could be filled from this cylinder? (Hint: find the number of moles of argon in each container.)

Answer available at the end of this section.

Using the Ideal Gas Law to Calculate Gas Densities and Molar Masses

The ideal gas law can also be used to calculate molar masses of gases from experimentally measured gas densities. To see how this is possible, we first rearrange the ideal gas law to obtain

$$\frac{n}{V} = \frac{P}{RT} \tag{10.4.9}$$

The left side has the units of moles per unit volume (mol/L). The number of moles of a substance equals its mass (m, in grams) divided by its molar mass (M, in grams per mole):

$$n = \frac{m}{M} \tag{10.4.10}$$

Substituting this expression for n into Equation 10.4.9 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{10.4.11}$$

Because m/V is the density d of a substance, we can replace m/V by d and rearrange to give

$$\rho = \frac{m}{V} = \frac{MP}{RT} \tag{10.4.12}$$

The distance between particles in gases is large compared to the size of the particles, so their densities are much lower than the densities of liquids and solids. Consequently, gas density is usually measured in grams per liter (g/L) rather than grams per milliliter (g/mL).

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Example 10.4.5

Calculate the density of butane at 25°C and a pressure of 750 mmHg.

Given: compound, temperature, and pressure

Asked for: density

Strategy:

A. Calculate the molar mass of butane and convert all quantities to appropriate units for the value of the gas constant.
B. Substitute these values into Equation 10.4.12 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$M = (4)(12.011) + (10)(1.0079) = 58.123\text{g/mol}$$

Using 0.08206 (L•atm)/(K•mol) for *R* means that we need to convert the temperature from degrees Celsius to kelvins (*T* = 25 + 273 = 298 K) and the pressure from millimeters of mercury to atmospheres:

$$P = 750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.987 \text{ atm}$$

B Substituting these values into Equation 10.4.12 gives

$$\rho = \frac{58.123 \text{ g/mol} \times 0.987 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} = 2.35 \text{ g/L}$$

Exercise 10.4.5: Density of Radon

Radon (Rn) is a radioactive gas formed by the decay of naturally occurring uranium in rocks such as granite. It tends to collect in the basements of houses and poses a significant health risk if present in indoor air. Many states now require that houses be tested for radon before they are sold. Calculate the density of radon at 1.00 atm pressure and 20°C and compare it with the density of nitrogen gas, which constitutes 80% of the atmosphere, under the same conditions to see why radon is found in basements rather than in attics.

Answer available at the end of this section.

A common use of Equation 10.4.12 is to determine the molar mass of an unknown gas by measuring its density at a known temperature and pressure. This method is particularly useful in identifying a gas that has been produced in a reaction, and it is not difficult to carry out. A flask or glass bulb of known volume is carefully dried, evacuated, sealed, and weighed empty. It is then filled with a sample of a gas at a known temperature and pressure and reweighed. The difference in mass between the two readings is the mass of the gas. The volume of the flask is usually determined by weighing the flask when empty and when filled with a liquid of known density such as water. The use of density measurements to calculate molar masses is illustrated in Example 10.4.6.

Example 10.4.6

The reaction of a copper penny with nitric acid results in the formation of a red-brown gaseous compound containing nitrogen and oxygen. A sample of the gas at a pressure of 727 mmHg and a temperature of 18°C weighs 0.289 g in a flask with a volume of 157.0 mL. Calculate the molar mass of the gas and suggest a reasonable chemical formula for the compound.

Given: pressure, temperature, mass, and volume

Asked for: molar mass and chemical formula

Strategy:

A. Solve Equation 10.4.12 for the molar mass of the gas and then calculate the density of the gas from the information given.
B. Convert all known quantities to the appropriate units for the gas constant being used. Substitute the known values into your equation and solve for the molar mass.
C. Propose a reasonable empirical formula using the atomic masses of nitrogen and oxygen and the calculated molar mass of the gas.

Solution:

A Solving Equation 10.4.12 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P}$$

Density is the mass of the gas divided by its volume:

$$\rho = \frac{m}{V} = \frac{0.289\text{g}}{0.157\text{L}} = 1.84\text{g/L}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K$$

$$P = 727\,mmHg \times \frac{1\text{atm}}{760\text{mmHg}} = 0.957\text{atm}$$

The molar mass of the unknown gas is thus

$$M = \frac{1.84\text{ g/L} \times 0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}} \times 291\text{ K}}{0.957\text{ atm}} = 45.9\text{g/mol}$$

C The atomic masses of N and O are approximately 14 and 16, respectively, so we can construct a list showing the masses of possible combinations:

$$M(\text{NO}) = 14 + 16 = 30\text{ g/mol}$$

$$M(\text{N}_2\text{O}) = (2)(14) + 16 = 44\text{ g/mol}$$

$$M(\text{NO}_2) = 14 + (2)(16) = 46\text{ g/mol}$$

The most likely choice is NO_2 which is in agreement with the data. The red-brown color of smog also results from the presence of NO_2 gas.

Exercise 10.4.6

You are in charge of interpreting the data from an unmanned space probe that has just landed on Venus and sent back a report on its atmosphere. The data are as follows: pressure, 90 atm; temperature, 557°C; density, 58 g/L. The major constituent of the atmosphere (>95%) is carbon. Calculate the molar mass of the major gas present and identify it.

Answer available at the end of this section.

Summary

The ideal gas law is derived from empirical relationships among the pressure, the volume, the temperature, and the number of moles of a gas; it can be used to calculate any of the four properties if the other three are known.

Ideal gas equation: $PV = nRT$,

where $R = 0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}} = 8.3145\frac{\text{J}}{\text{K}\cdot\text{mol}}$

General gas equation: $\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$

Density of a gas: $\rho = \frac{MP}{RT}$

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the **ideal gas law**, *PV* = *nRT*. The proportionality constant, *R*, is called the **gas constant** and has the value 0.08206 (L•atm)/(K•mol), 8.3145 J/(K•mol), or 1.9872 cal/(K•mol), depending on the units used. The ideal gas law describes the behavior of an **ideal gas**, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. **Standard temperature and pressure (STP)** is 0°C and 1 atm. The volume of 1 mol of an ideal gas at STP is 22.41 L, the **standard molar volume**. All of the empirical gas relationships are special cases of the ideal gas law in which two of the four parameters are held constant. The ideal gas law allows us to calculate the value of the fourth quantity (*P*, *V*, *T*, or *n*) needed to describe a gaseous sample when the others are known and also predict the value of these quantities following a change in conditions if the original conditions (values of *P*, *V*, *T*, and *n*) are known. The ideal gas law can also be used to calculate the density of a gas if its molar mass is known or, conversely, the molar mass of an unknown gas sample if its density is measured.

Answers

Exercise 10.4.1

1.5 atm

Exercise 10.4.2

0.52 L

Exercise 10.4.3

23.4 atm

Exercise 10.4.4

4.07×10^3

Exercise 10.4.5**: Density of Radon**

radon, 9.23 g/L; N_2, 1.17 g/L

Exercise 10.4.6

44 g/mol; CO_2

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10.5: Further Applications of the Ideal-Gas Equations

Learning Objectives

- To relate the amount of gas consumed or released in a chemical reaction to the stoichiometry of the reaction.
- To understand how the ideal gas equation and the stoichiometry of a reaction can be used to calculate the volume of gas produced or consumed in a reaction.

With the ideal gas law, we can use the relationship between the amounts of gases (in moles) and their volumes (in liters) to calculate the stoichiometry of reactions involving gases, if the pressure and temperature are known. This is important for several reasons. Many reactions that are carried out in the laboratory involve the formation or reaction of a gas, so chemists must be able to quantitatively treat gaseous products and reactants as readily as they quantitatively treat solids or solutions. Furthermore, many, if not most, industrially important reactions are carried out in the gas phase for practical reasons. Gases mix readily, are easily heated or cooled, and can be transferred from one place to another in a manufacturing facility via simple pumps and plumbing.

Gas Densities and Molar Mass

The ideal-gas equation can be manipulated to solve a variety of different types of problems. For example, the density, ρ, of a gas, depends on the number of gas molecules in a constant volume. To determine this value, we rearrange the ideal gas equation to

$$\frac{n}{V} = \frac{P}{RT} \tag{10.5.1}$$

Density of a gas is generally expressed in g/L (mass over volume). Multiplication of the left and right sides of Equation 10.5.1 by the molar mass in g/mol (M) of the gas gives

$$\rho = \frac{g}{L} = \frac{PM}{RT} \tag{10.5.2}$$

This allows us to determine the density of a gas when we know the molar mass, or vice versa.

The density of a gas INCREASES with increasing pressure and DECREASES with increasing temperature

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Example 10.5.1

What is the density of nitrogen gas (N_2) at 248.0 Torr and 18° C?

Solution

Step 1: Write down your given information

- P = 248.0 Torr

- V = ?
- n = ?
- R = 0.0820574 L•atm•mol^{-1} K^{-1}
- T = 18° C

Step 2: Convert as necessary.

$$(248\ \text{Torr}) \times \frac{1\ \text{atm}}{760\ \text{Torr}} = 0.3263\ \text{atm}$$

$$18\,^{o}C + 273 = 291K$$

Step 3: This one is tricky. We need to manipulate the Ideal Gas Equation to incorporate density into the equation.

Write down all known equations:

$$PV = nRT$$

$$\rho = \frac{m}{V}$$

where ρ is density, m is mass, and V is volume.

$$m = M \times n$$

where M is molar mass and n is the number of moles.

Now take the definition of density (Equation 10.5.1)

$$\rho = \frac{m}{V}$$

Keeping in mind $m = M \times n$...replace $(M \times n)$ for $mass$ within the density formula.

$$\rho = \frac{M \times n}{V}$$

$$\frac{\rho}{M} = \frac{n}{V}$$

Now manipulate the Ideal Gas Equation

\[\begin{align*} PV &= nRT \[4pt] \dfrac{n}{V} &= \dfrac{P}{RT} \end{align*} \nonumber \]

(n/V) is in both equations.

$$\frac{n}{V} = \frac{\rho}{M}$$

$$= \frac{P}{RT}$$

Now combine them please.

$$\frac{\rho}{M} = \frac{P}{RT}$$

Isolate density.

$$\rho = \frac{PM}{RT}$$

Step 4: Now plug in the information you have.

$$\begin{aligned}\rho &= \frac{PM}{RT} \\ &= \frac{(0.3263\ \text{atm})(2 * 14.01\ \text{g/mol})}{(0.08206\ L\,atm/K mol)(291\ \text{K})} \\ &= 0.3828\ g/L\end{aligned}$$

An example of varying density for a useful purpose is the hot air balloon, which consists of a bag (called the envelope) that is capable of containing heated air. As the air in the envelope is heated, it becomes less dense than the surrounding cooler air (Equation 10.5.2), which is has enough lifting power (due to buoyancy) to cause the balloon to float and rise into the air. Constant heating of the air is required to keep the balloon aloft. As the air in the balloon cools, it contracts, allowing outside cool air to enter, and the density increases. When this is carefully controlled by the pilot, the balloon can land as gently as it rose.



Figure 10.5.1: A hot air balloon is inflated partially with cold air from a gas-powered fan, before the propane burners are used for final inflation.

Determining Gas Volumes in Chemical Reactions

The ideal gas law can be used to calculate volume of gases consumed or produced. The ideal-gas equation frequently is used to interconvert between volumes and molar amounts in chemical equations.

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Example 10.5.2A

What volume of carbon dioxide gas is produced at STP by the decomposition of 0.150 g $\mathrm{CaCO_3}$ via the equation:

$$\mathrm{CaCO_3\,(s)\ \rightarrow CaO\,(s) + CO_2\,(g)}$$

Solution

Begin by converting the mass of calcium carbonate to moles.

$$\frac{0.150\ g}{100.1\ g/mol} = 0.00150\ mol$$

The stoichiometry of the reaction dictates that the number of moles $\mathrm{CaCO_3}$ decomposed equals the number of moles $\mathrm{CO_2}$ produced. Use the ideal-gas equation to convert moles of $\mathrm{CO_2}$ to a volume.

$$\begin{aligned} V &= \frac{nRT}{PR} \\ &= \frac{(0.00150\ mol)\left(0.08206\ \frac{L \cdot atm}{mol \cdot K}\right)(273.15\ K)}{1\ atm} \\ &= 0.0336\ L\ or\ 33.6\ mL \end{aligned}$$

Example $10.5.2B$

A 3.00 L container is filled with $\mathrm{Ne(g)}$ at 770 mmHg at 27°C. A $0.633\ \mathrm{g}$ sample of $\mathrm{CO_2}$ vapor is then added.

- What is the partial pressure of $\mathrm{CO_2}$ and Ne in atm?
- What is the total pressure in the container in atm?

Solution

Step 1: Write down all given information, and convert as necessary.

Before:

- \(P = 770\,mmHg \rigtharrow 1.01 \,atm \nonumber \]
- $V = 3.00\ L$
- $n_{\mathrm{Ne}} = ?$
- $T = 27^oC \rightarrow 300\ K$

Other Unknowns: $n_{\mathrm{CO_2}}$= ?

$$n_{CO_2} = 0.633\ \mathrm{g\ CO_2} \times \frac{1\ \mathrm{mol}}{44\ \mathrm{g}} = 0.0144\ \mathrm{mol\ CO_2}$$

Step 2: After writing down all your given information, find the unknown moles of Ne**.**

$$\begin{aligned} n_{Ne} &= \frac{PV}{RT} \\ &= \frac{(1.01\ \mathrm{atm})(3.00\ \mathrm{L})}{(0.08206\ atm\ L/mol\ K)(300\ \mathrm{K})} \\ &= 0.123\ \mathrm{mol} \end{aligned}$$

Because the pressure of the container before the $\mathrm{CO_2}$ was added contained only Ne, that is your partial pressure of Ne. After converting it to atm, you have already answered part of the question!

$$P_{Ne} = 1.01\ \mathrm{atm}$$

Step 3: Now that have pressure for Ne, you must find the partial pressure for CO_2. Use the ideal gas equation.

$$\frac{P_{Ne}\cancel{V}}{n_{Ne}\cancel{RT}} = \frac{P_{CO_2}\cancel{V}}{n_{CO_2}\cancel{RT}}$$

but because both gases share the same Volume (V) and Temperature (T) and since the Gas Constant (R) is constants, all three terms cancel.

$$\frac{P}{n_{Ne}} = \frac{P}{n_{CO_2}}$$

$$\frac{1.01 \text{ atm}}{0.123 \text{ mol Ne}} = \frac{P_{CO_2}}{0.0144 \text{ mol } CO_2}$$

$$P_{CO_2} = 0.118 \text{ atm}$$

This is the partial pressure CO_2.

Step 4: Now find total pressure.

$$\begin{aligned} P_{total} &= P_{Ne} + P_{CO_2} \\ &= 1.01 \text{ atm} + 0.118 \text{ atm} \\ &= 1.128 \text{ atm} \\ &\approx 1.13 \text{ atm (with appropriate significant figures)} \end{aligned}$$

Example $10.5.2C$: Sulfuric Acid

Sulfuric acid, the industrial chemical produced in greatest quantity (almost 45 million tons per year in the United States alone), is prepared by the combustion of sulfur in air to give SO_2, followed by the reaction of SO_2 with O_2 in the presence of a catalyst to give SO_3, which reacts with water to give H_2SO_4. The overall chemical equation is as follows:

$$2\,S\,(s) + 3\,O_2\,(g) + 2\,H_2O\,(l) \rightarrow 2\,H_2SO_4\,(aq)$$

What volume of O_2 (in liters) at 22°C and 745 mmHg pressure is required to produce 1.00 ton (907.18 kg) of H_2SO_4?

Given: reaction, temperature, pressure, and mass of one product

Asked for: volume of gaseous reactant

Strategy:

A Calculate the number of moles of H_2SO_4 in 1.00 ton. From the stoichiometric coefficients in the balanced chemical equation, calculate the number of moles of O_2 required.

B Use the ideal gas law to determine the volume of O_2 required under the given conditions. Be sure that all quantities are expressed in the appropriate units.

Solution:

$$\text{mass of } H_2SO_4 \rightarrow \text{moles } H_2SO_4 \rightarrow \text{moles } O_2 \rightarrow \text{liters } O_2$$

A We begin by calculating the number of moles of H_2SO_4 in 1.00 ton:

$$\frac{907.18 \times 10^3 \text{ g } H_2SO_4}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } H_2SO_4$$

We next calculate the number of moles of O_2 required:

$$9250 \text{ mol } H_2SO_4 \times \frac{3 \text{mol } O_2}{2 \text{mol } H_2SO_4} = 1.389 \times 10^4 \text{ mol } O_2$$

B After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of O_2:

$$V = \frac{nRT}{P}$$

$$= \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}$$

$$= 3.43 \times 10^5 \text{ L}$$

The answer means that more than 300,000 L of oxygen gas are needed to produce 1 ton of sulfuric acid. These numbers may give you some appreciation for the magnitude of the engineering and plumbing problems faced in industrial chemistry.

Exercise 10.5.2

Charles used a balloon containing approximately 31,150 L of H_2 for his initial flight in 1783. The hydrogen gas was produced by the reaction of metallic iron with dilute hydrochloric acid according to the following balanced chemical equation:

$$\text{Fe}\,(\text{s}) + 2\,\text{HCl}\,(\text{aq}) \rightarrow \text{H}_2\,(\text{g}) + \text{FeCl}_2\,(\text{aq})$$

How much iron (in kilograms) was needed to produce this volume of H_2 if the temperature were 30°C and the atmospheric pressure was 745 mmHg?

Answer available at the end of this section.

Example 10.5.3: Emergency Air bags

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2\,\text{NaN}_3 \rightarrow 2\,\text{Na}\,(\text{s}) + 3\,\text{N}_2\,(\text{g})$$

This reaction is used to inflate the air bags that cushion passengers during automobile collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. If the N_2 gas that results from the decomposition of a 5.00 g sample of NaN_3 could be collected by displacing water from an inverted flask, what volume of gas would be produced at 21°C and 762 mmHg?

Given: reaction, mass of compound, temperature, and pressure

Asked for: volume of nitrogen gas produced

Strategy:

A Calculate the number of moles of N_2 gas produced. From the data in Table S3, determine the partial pressure of N_2 gas in the flask.

B Use the ideal gas law to find the volume of N_2 gas produced.

Solution:

A Because we know the mass of the reactant and the stoichiometry of the reaction, our first step is to calculate the number of moles of N_2 gas produced:

$$\frac{5.00 \text{ g } \text{NaN}_3}{(22.99 + 3 \times 14.01) \text{ g/mol}} \times \frac{3 \text{mol } \text{N}_2}{2 \text{mol } \text{NaN}_3} = 0.115 \text{ mol } \text{N}_2$$

The pressure given (762 mmHg) is the *total* pressure in the flask, which is the sum of the pressures due to the N_2 gas and the water vapor present. Table S3 tells us that the vapor pressure of water is 18.65 mmHg at 21°C (294 K), so the partial pressure of the N_2 gas in the flask is only

$$(762 - 18.65)\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 743.4\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}}$$

$$= 0.978\ atm.$$

B Solving the ideal gas law for *V* and substituting the other quantities (in the appropriate units), we get

$$V = \frac{nRT}{P} = \frac{0.115\ \text{mol} \times 0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 294\ \text{K}}{0.978\ \text{atm}} = 2.84\ \text{L}$$

Exercise10.5.3

A 1.00 g sample of zinc metal is added to a solution of dilute hydrochloric acid. It dissolves to produce H_2 gas according to the equation

$$\text{Zn}\,(\text{s}) + 2\,\text{HCl}\,(\text{aq}) \longrightarrow \text{H}_2\,(\text{g}) + \text{ZnCl}_2\,(\text{aq}).$$

The resulting H_2 gas is collected in a water-filled bottle at 30°C and an atmospheric pressure of 760 mmHg. What volume does it occupy?

Answer available at the end of this section.

Summary

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can then be calculated from the volume of water displaced and the atmospheric pressure. A gas collected in such a way is not pure, however, but contains a significant amount of water vapor. The measured pressure must therefore be corrected for the vapor pressure of water, which depends strongly on the temperature.

Answers

Exercise 10.5.2

68.6 kg of Fe (approximately 150 lb)

Exercise10.5.3

0.397 L

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10.6: Gas Mixtures and Partial Pressures

Learning Objectives

- To determine the contribution of each component gas to the total pressure of a mixture of gases

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{10.6.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressure, the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, ***the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases***. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as *Dalton's law of partial pressures*. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots \tag{10.6.2}$$

$$= \sum_{i=1}^{n} P_i \tag{10.6.3}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

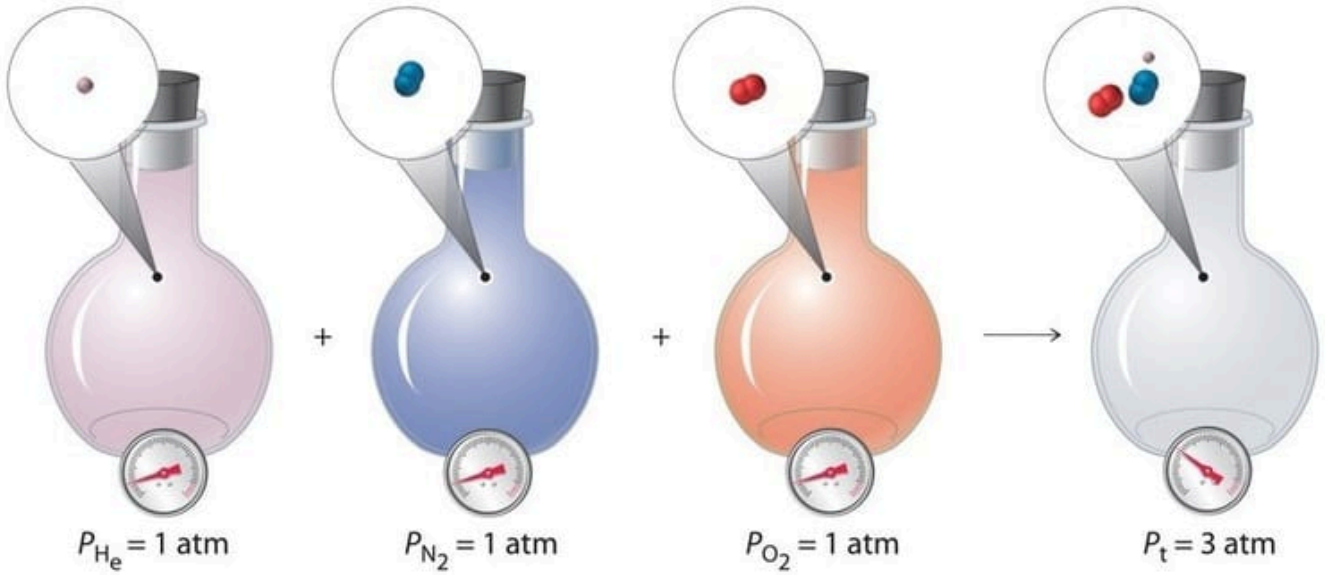


Figure 10.6.1: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B \tag{10.6.4}$$

$$= n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) \tag{10.6.5}$$

$$= (n_A + n_B)\left(\frac{RT}{V}\right) \tag{10.6.6}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (n_1 + n_2 + n_3 + \cdots + n_n)\left(\frac{RT}{V}\right) \tag{10.6.7}$$

$$= \sum_{i=1}^{n} n_i\left(\frac{RT}{V}\right) \tag{10.6.8}$$

Equation 10.6.8 restates Equation 10.6.6 in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on only the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For Equation 10.6.8 to be valid, the identity of the particles present cannot have an effect. Thus an ideal gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 10.6.1.

Example 10.6.1: The Bends

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called "the bends." At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of components, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A. Calculate the number of moles of He and $\mathrm{O_2}$ present.

B. Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of He is

$$n_{\mathrm{He}} = \frac{326.4\ \mathrm{g}}{4.003\ \mathrm{g/mol}} = 81.54\ \mathrm{mol}$$

The number of moles of $\mathrm{O_2}$ is

$$n_{\mathrm{O_2}} = \frac{51.2\ \mathrm{g}}{32.00\ \mathrm{g/mol}} = 1.60\ \mathrm{mol}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\mathrm{He}} = \frac{n_{\mathrm{He}}RT}{V} = \frac{81.54\ \mathrm{mol} \times 0.08206\ \frac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 293.15\ \mathrm{K}}{10.0\ \mathrm{L}} = 196.2\ \mathrm{atm}$$

$$P_{\mathrm{O_2}} = \frac{n_{\mathrm{O_2}}RT}{V} = \frac{1.60\ \mathrm{mol} \times 0.08206\ \frac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 293.15\ \mathrm{K}}{10.0\ \mathrm{L}} = 3.85\ \mathrm{atm}$$

The total pressure is the sum of the two partial pressures:

$$P_{\mathrm{tot}} = P_{\mathrm{He}} + P_{\mathrm{O_2}} = (196.2 + 3.85)\ \mathrm{atm} = 200.1\ \mathrm{atm}$$

Exercise 10.6.1

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer available at the end of this section.

Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction (χ) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_{tot}):

$$\chi_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{10.6.9}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $\chi_A = 1.0$, then the sample is pure A, not a mixture. If $\chi_A = 0$, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let's evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the ideal gas law to describe the pressures of both gas A and the mixture: $P_A = n_A RT/V$ and $P_{tot} = n_t RT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = \chi_A \tag{10.6.10}$$

Rearranging this equation gives

$$P_A = \chi_A P_{tot} \tag{10.6.11}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. By volume, Earth's atmosphere is about 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of gases such as CO_2, H_2O, and others. This means that 78% of the particles present in the atmosphere are N_2; hence the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using Equation 10.6.11, we therefore know that the partial pressure of N_2 is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of O_2 and Ar are 0.21 and 0.009 atm, respectively.

YouTube Video

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Example 10.6.2: Exhaling Composition

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

the mole fractions of the gases

	Inhaled Air / mmHg	Exhaled Air / mmHg
$P_{\mathrm{N_2}}$	597	568
$P_{\mathrm{O_2}}$	158	116
$P_{\mathrm{H_2O}}$	0.3	28
$P_{\mathrm{CO_2}}$	5	48
P_{Ar}	8	8
P_{tot}	767	767

Given: pressures of gases in inhaled and exhaled air

Asked for: mole fractions of gases in exhaled air

Strategy:

Calculate the mole fraction of each gas using Equation 10.6.11.

Solution:

The mole fraction of any gas A is given by

$$\chi_A = \frac{P_A}{P_{tot}}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of $\mathrm{CO_2}$ is given as:

$$\chi_{\mathrm{CO_2}} = \frac{48\ \mathrm{mmHg}}{767\ \mathrm{mmHg}} = 0.063$$

The following table gives the values of χ_A for the gases in the exhaled air.

Solutions to Example 10.6.2

Gas	Mole Fraction
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

Exercise 10.6.2

Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.

Answer available at the end of this section.

Summary

The partial pressure of each gas in a mixture is proportional to its mole fraction. The pressure exerted by each gas in a gas mixture (its **partial pressure**) is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (**Dalton's law of partial pressures**). The amount of gas present in a mixture may be described by its partial pressure or its mole fraction. The **mole fraction** of any component of a mixture is the ratio of the number of moles of that substance to the total number of moles of all substances present. In a mixture of gases, the partial pressure of each gas is the product of the total pressure and the mole fraction of that gas.

Answers

Exercise 10.6.1

$P_{CH_4} = 137\ \ atm$; $P_{C_2H_6} = 13.4\ \ atm$; $P_{tot} = 151\ \ atm$

Exercise 10.6.2

$$P_{CO_2} = 86 \text{ atm}$$
$$P_{N_2} = 2.7 \text{ atm}$$

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10.7: Kinetic-Molecular Theory

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

A Molecular Description

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

five postulates of Kinetic Molecular Theory

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In the following sections, we explain how this theory must be modified to account for the behavior of real gases.

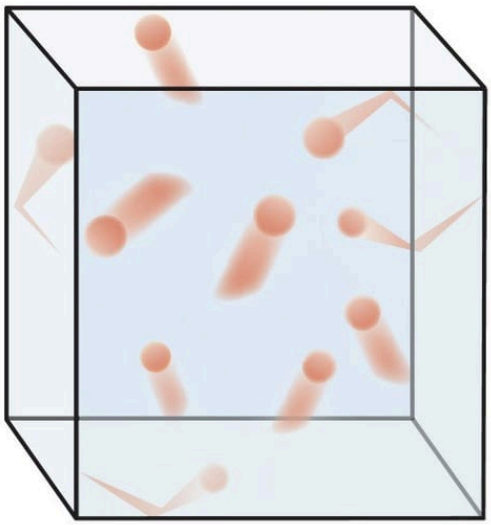


Figure 10.7.1: Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 10.7.2).

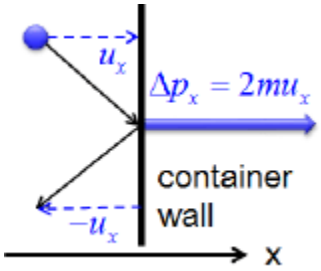


Figure 10.7.2: Momentum transfer (impulse) from a molecule to the container wall as it bounces off the wall. u_x and Δp_x are the x component of the molecular velocity and the momentum transferred to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity u_x in x direction hits is expressed as:

$$\Delta p_x = 2mu_x \tag{10.7.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (u_x) \times \left(\frac{N}{V}\right) \tag{10.7.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mu_x^2 \tag{10.7.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace u_x^2 in the expression above with the average value of u_x^2, which is denoted by $\overline{u_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\overline{u_x^2} \tag{10.7.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{u^2}.$$

Here the quantity $\overline{u^2}$ is called the **mean-square speed** defined as the average value of square-speed (u^2) over all molecules. Since

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

for each molecule, then

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}.$$

By substituting $\frac{1}{3}\overline{u^2}$ for $\overline{u_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2} \tag{10.7.5}$$

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Postulate 5 refers to the *average translational* kinetic energy of the molecules of a gas ($\overline{e_K}$), which can be represented as *and states that at a given Kelvin temperature* (T)*, all gases have the same value of*

$$\overline{e_K} = \frac{1}{2} m\overline{u^2} = \frac{3}{2}\frac{R}{N_A} T \tag{10.7.6}$$

where N_A is the Avogadro's constant. The total translational kinetic energy of 1 mole of molecules can be obtained by multiplying the equation by N_A:

$$N_A\overline{e_K} = \frac{1}{2} M\overline{u^2} = \frac{3}{2} RT \tag{10.7.7}$$

where M is the molar mass of the gas molecules and is related to the molecular mass by $M = N_A m$. By rearranging the equation, we can get the relationship between the root-mean square speed (u_{rms}) and the temperature. The rms speed (u_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{10.7.8}$$

where N is the number of particles and u_i is the speed of particle i.

The relationship between u_{rms} and the temperature is given by:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{10.7.9}$$

In Equation 10.7.9, u_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol). Equation 10.7.9 shows that u_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however,

because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, not the same average speed. In contrast, the most probable speed (vp) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then Equation 10.7.8 tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and vp increases.

At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.

Example 10.7.1

The speeds of eight particles were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{av}) root mean square speed (v_{rms}), and most probable speed (v_{m}).

Given: particle speeds

Asked for: average speed (v_{av}), root mean square speed (v_{rms}), and most probable speed (v_{m})

Strategy:

Use Equation 10.7.6 to calculate the average speed and Equation 10.7.8 to calculate the rms speed. Find the most probable speed by determining the speed at which the greatest number of particles is moving.

Solution:

The average speed is the sum of the speeds divided by the number of particles:

$$v_{\text{av}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\text{rms}} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}} = 6.2\ \text{m/s}$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence $v_{\text{m}} = 6.0$ m/s. The v_{rms} of the particles, which is related to the average kinetic energy, is greater than their average speed.

Boltzmann Distributions

At any given time, what fraction of the molecules in a particular sample has a given speed? Some of the molecules will be moving more slowly than average, and some will be moving faster than average, but how many in each situation? Answers to questions such as these can have a substantial effect on the amount of product formed during a chemical reaction. This problem was solved mathematically by Maxwell in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature. Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in Figure 10.7.3. Increasing the temperature has two effects. First, the peak of the curve moves to the right because the most probable speed increases. Second, the curve becomes broader because of the increased spread of the speeds. Thus increased temperature increases the *value* of the most probable speed but decreases the relative number of molecules that have that speed. Although the mathematics behind curves such as those in Figure 10.7.3 were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributions, after one of the other major figures responsible for the kinetic molecular theory of gases.

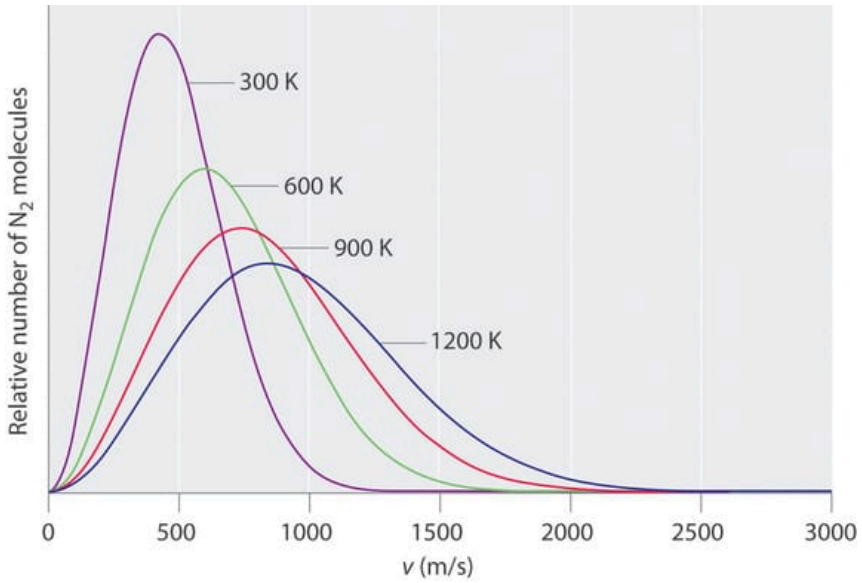


Figure 10.7.3: The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

The Relationships among Pressure, Volume, and Temperature

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

- **Pressure versus Volume**: At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.
- **Volume versus Temperature**: Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the pressure, as we have just seen. Thus an increase in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.
- **Pressure of Gas Mixtures**: Postulate 3 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton's law of partial pressures holds.

Example 10.7.2

The temperature of a 4.75 L container of N_2 gas is increased from 0°C to 117°C. What is the qualitative effect of this change on the

a. average kinetic energy of the N_2 molecules?
b. rms speed of the N_2 molecules?
c. average speed of the N_2 molecules?
d. impact of each N_2 molecule on the wall of the container during a collision with the wall?
e. total number of collisions per second of N_2 molecules with the walls of the entire container?
f. number of collisions per second of N_2 molecules with each square centimeter of the container wall?
g. pressure of the N_2 gas?

Given: temperatures and volume

Asked for: effect of increase in temperature

Strategy:

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

Solution:

a. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
b. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
c. If the rms speed of the N_2 molecules increases, the average speed also increases.
d. If, on average, the particles are moving faster, then they strike the container walls with more energy.
e. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
f. The number of collisions per second of N_2 molecules with each square centimeter of container wall increases because the total number of collisions has increased, but the volume occupied by the gas and hence the total area of the walls are unchanged.
g. The pressure exerted by the N_2 gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law.

Exercise 10.7.2

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at constant temperature. What is the qualitative effect of this change on the

a. average kinetic energy of the He atoms?
b. rms speed of the He atoms?
c. average speed of the He atoms?
d. impact of each He atom on the wall of the container during a collision with the wall?
e. total number of collisions per second of He atoms with the walls of the entire container?
f. number of collisions per second of He atoms with each square centimeter of the container wall?
g. pressure of the He gas?

Answer a available at the end of this section.

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Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T n$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}$$

- **Kinetic molecular theory of gases:**

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

The behavior of ideal gases is explained by the **kinetic molecular theory of gases**. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same **root mean square (rms) speed (v_{rms})**. The actual values of speed and kinetic energy are not the same for all particles of a gas but are given by a **Boltzmann distribution**, in which some molecules have higher or lower speeds (and kinetic energies) than average.

Answers

Exercise 10.7.2

no change
no change
no change
no change
decreases
decreases
decreases

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10.8: Molecular Effusion and Diffusion

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

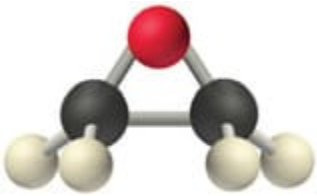
Diffusion and Effusion

As you have learned, the molecules of a gas are *not* stationary but in constant and random motion. If someone opens a bottle of perfume in the next room, for example, you are likely to be aware of it soon. Your sense of smell relies on molecules of the aromatic substance coming into contact with specialized olfactory cells in your nasal passages, which contain specific receptors (protein molecules) that recognize the substance. How do the molecules responsible for the aroma get from the perfume bottle to your nose? You might think that they are blown by drafts, but, in fact, molecules can move from one place to another even in a draft-free environment.

Diffusion is the gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with uniform composition. Diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. The related process, **effusion**, is the escape of gaseous molecules through a small (usually microscopic) hole, such as a hole in a balloon, into an evacuated space.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass. This relationship *is referred to as Graham's law*, after the Scottish chemist Thomas Graham (1805–1869). The ratio of the effusion rates of two gases is the square root of the inverse ratio of their molar masses:

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}} \tag{10.8.1}$$



Ethylene oxide

Helium (M = 4.00 g/mol) effuses much more rapidly than ethylene oxide (M = 44.0 g/mol). Because helium is less dense than air, helium-filled balloons "float" at the end of a tethering string. Unfortunately, rubber balloons filled with helium soon lose their buoyancy along with much of their volume. In contrast, rubber balloons filled with air tend to retain their shape and volume for a much longer time. Because helium has a molar mass of 4.00 g/mol, whereas air has an average molar mass of about 29 g/mol, pure helium effuses through the microscopic pores in the rubber balloon $\sqrt{\frac{29}{4.00}} = 2.7$ times faster than air. For this reason, high-quality helium-filled balloons are usually made of Mylar, a dense, strong, opaque material with a high molecular mass that forms films that have many fewer pores than rubber. Hence, mylar balloons can retain their helium for days.

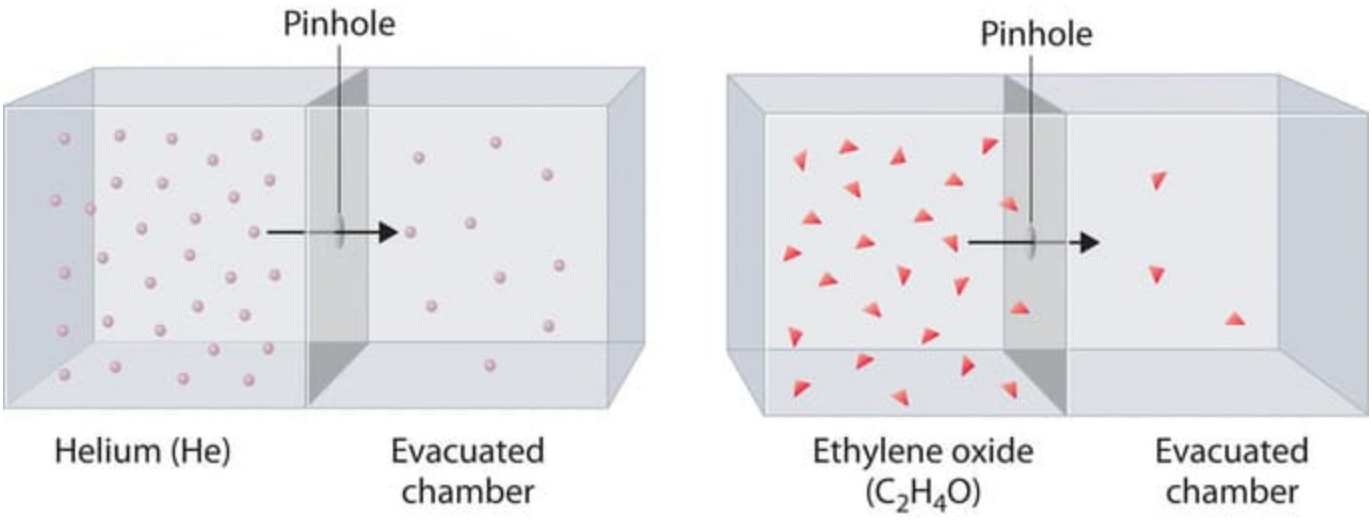


Figure 10.8.1: The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law (Equation 10.8.1).

At a given temperature, heavier molecules move more slowly than lighter molecules.

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Example 10.8.1

During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of ^{235}U. Naturally occurring uranium is only 0.720% ^{235}U, whereas most of the rest (99.275%) is ^{238}U, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

1. Calculate the ratio of the rates of effusion of $^{235}UF_6$ and $^{238}UF_6$ for a single step in which UF_6 is allowed to pass through a porous barrier. (The atomic mass of ^{235}U is 235.04, and the atomic mass of ^{238}U is 238.05.)
2. If n identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the nth power. How many effusion steps are needed to obtain 99.0% pure $^{235}UF_6$?

Given: isotopic content of naturally occurring uranium and atomic masses of ^{235}U and ^{238}U

Asked for: ratio of rates of effusion and number of effusion steps needed to obtain 99.0% pure $^{235}UF_6$

Strategy:

A. Calculate the molar masses of $^{235}UF_6$ and $^{238}UF_6$, and then use Graham's law to determine the ratio of the effusion rates. Use this value to determine the isotopic content of $^{235}UF_6$ after a single effusion step.

B. Divide the final purity by the initial purity to obtain a value for the number of separation steps needed to achieve the desired purity. Use a logarithmic expression to compute the number of separation steps required.

Solution:

A The first step is to calculate the molar mass of UF_6 containing ^{235}U and ^{238}U. Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998. The molar mass of $^{235}UF_6$ is

$$234.04 + (6)(18.998) = 349.03 \text{ g/mol}$$

The molar mass of $^{238}UF_6$ is

$$238.05 + (6)(18.998) = 352.04 \text{ g/mol}$$

The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law using Equation 10.8.1:

$$\frac{\text{rate } ^{235}\text{UF}_6}{\text{rate } ^{238}\text{UF}_6} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} = 1.0043$$

B To obtain 99.0% pure $^{235}UF_6$ requires many steps. We can set up an equation that relates the initial and final purity to the number of times the separation process is repeated:

final purity = (initial purity)(separation)^n

In this case, 0.990 = (0.00720)(1.0043)^n, which can be rearranged to give

$$1.0043^n = \frac{0.990}{0.00720} = 137.50$$

Taking the logarithm of both sides gives

$$n \ln(1.0043) = \ln(137.50) \tag{10.8.2}$$

$$n = \frac{\ln(137.50)}{\ln(1.0043)} \tag{10.8.3}$$

$$= 1148 \tag{10.8.4}$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched ^{235}U. Below is a small part of a system that is used to prepare enriched uranium on a large scale.



A Portion of a Plant for Separating Uranium Isotopes by Effusion of UF_6. The large cylindrical objects (note the human for scale) are so-called diffuser (actually effuser) units, in which gaseous UF_6 is pumped through a porous barrier to partially separate the isotopes. The UF_6 must be passed through multiple units to become substantially enriched in ^{235}U.

Exercise 10.8.1

Helium consists of two isotopes: ^3He (natural abundance = 0.000134%) and ^4He (natural abundance = 99.999866%). Their atomic masses are 3.01603 and 4.00260, respectively. Helium-3 has unique physical properties and is used in the study of ultralow temperatures. It is separated from the more abundant ^4He by a process of gaseous effusion.

a. Calculate the ratio of the effusion rates of ^3He and ^4He and thus the enrichment possible in a single effusion step.
b. How many effusion steps are necessary to yield 99.0% pure ^3He?

Answer a available at the end of this section.

Rates of Diffusion or Effusion

Graham's law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have the same average kinetic energy. We can write the expression for the average kinetic energy of two gases with different molar masses:

$$KE = \frac{1}{2}\frac{M_\mathrm{A}}{N_A}v_{\mathrm{rms,A}}^2 = \frac{1}{2}\frac{M_\mathrm{B}}{N_A}v_{\mathrm{rms,B}}^2 \tag{10.8.5}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v_{\mathrm{rms,B}}^2}{v_{\mathrm{rms,A}}^2} = \frac{M_\mathrm{A}}{M_\mathrm{B}} \tag{10.8.6}$$

Taking the square root of both sides gives

$$\frac{v_{\mathrm{rms,B}}}{v_{\mathrm{rms,A}}} = \sqrt{\frac{M_\mathrm{A}}{M_\mathrm{B}}} \tag{10.8.7}$$

Thus the rate at which a molecule, or a mole of molecules, diffuses or effuses is directly related to the speed at which it moves.

Equation 10.8.7 shows that Graham's law is a direct consequence of the fact that gaseous molecules at the same temperature have the same average kinetic energy.

Typically, gaseous molecules have a speed of hundreds of meters per second (hundreds of miles per hour). The effect of molar mass on these speeds is dramatic, as illustrated in Figure 10.8.3 for some common gases. Because all gases have the same average kinetic energy, according to the Boltzmann distribution, molecules with lower masses, such as hydrogen and helium, have a wider distribution of speeds.

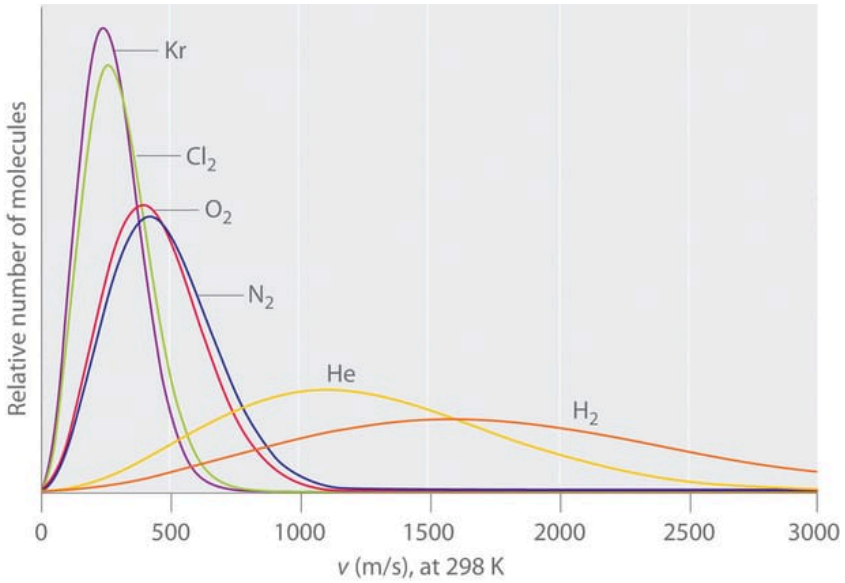


Figure 10.8.3: The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses

The lightest gases have a wider distribution of speeds and the highest average speeds.

> Molecules with lower masses have a wider distribution of speeds and a higher average speed.

Gas molecules do not diffuse nearly as rapidly as their very high speeds might suggest. If molecules actually moved through a room at hundreds of miles per hour, we would detect odors faster than we hear sound. Instead, it can take several minutes for us to detect an aroma because molecules are traveling in a medium with other gas molecules. Because gas molecules collide as often as 10^{10} times per second, changing direction and speed with each collision, they do not diffuse across a room in a straight line, as illustrated schematically in Figure 10.8.4.

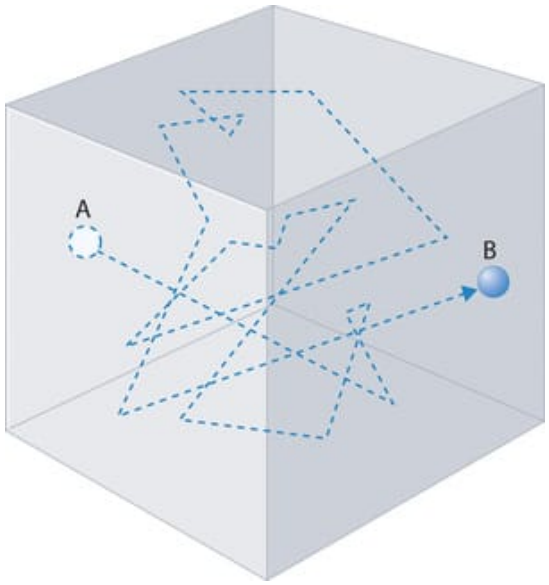


Figure 10.8.4: The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

The average distance traveled by a molecule between collisions is the mean free path. The denser the gas, the shorter the mean free path; conversely, as density decreases, the mean free path becomes longer because collisions occur less frequently. At 1 atm pressure and 25°C, for example, an oxygen or nitrogen molecule in the atmosphere travels only about 6.0×10^{-8} m (60 nm) between collisions. In the upper atmosphere at about 100 km altitude, where gas density is much lower, the mean free path is about 10 cm; in space between galaxies, it can be as long as 1×10^{10} m (about 6 million miles).

The **denser** the gas, the **shorter** the mean free path.

Example 10.8.2

Calculate the rms speed of a sample -butene (C_4H_8) at 20°C.

Given: compound and temperature

Asked for: rms speed

Strategy:

Calculate the molar mass of cis-2-butene. Be certain that all quantities are expressed in the appropriate units and then use Equation 10.8.5 to calculate the rms speed of the gas.

Solution:

To use Equation 10.8.4, we need to calculate the molar mass of *cis*-2-butene and make sure that each quantity is expressed in the appropriate units. Butene is C_4H_8, so its molar mass is 56.11 g/mol. Thus

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{10.8.8}$$

$$= \sqrt{\frac{3 \times 8.3145 \ \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (20 + 273) \ \text{K}}{56.11 \times 10^{-3} \ \text{kg}}} \tag{10.8.9}$$

$$= 361 \ m/s \tag{10.8.10}$$

or approximately 810 mi/h.

Exercise 10.8.1

Calculate the rms speed of a sample of radon gas at 23°C.

Answer available at the end of this section.

The kinetic molecular theory of gases demonstrates how a successful theory can explain previously observed empirical relationships (laws) in an intuitively satisfying way. Unfortunately, the actual gases that we encounter are not "ideal," although their behavior usually approximates that of an ideal gas.

Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T,$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}},$$

- **Kinetic molecular theory of gases**:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}.$$

- **Graham's law for effusion:**

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_{\text{A}}}{M_{\text{B}}}}$$

Diffusion is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, **effusion** is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (**Graham's law**), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases. The **mean free path** of a molecule is the average distance it travels between collisions.

Answers

Exercise 10.8.1

ratio of effusion rates = 1.15200; one step gives 0.000154% ^{3}He

96 steps

Exercise 10.8.1

$1.82 \times 10^2 \ m/s$ (about 410 mi/h)

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10.9: Real Gases - Deviations from Ideal Behavior

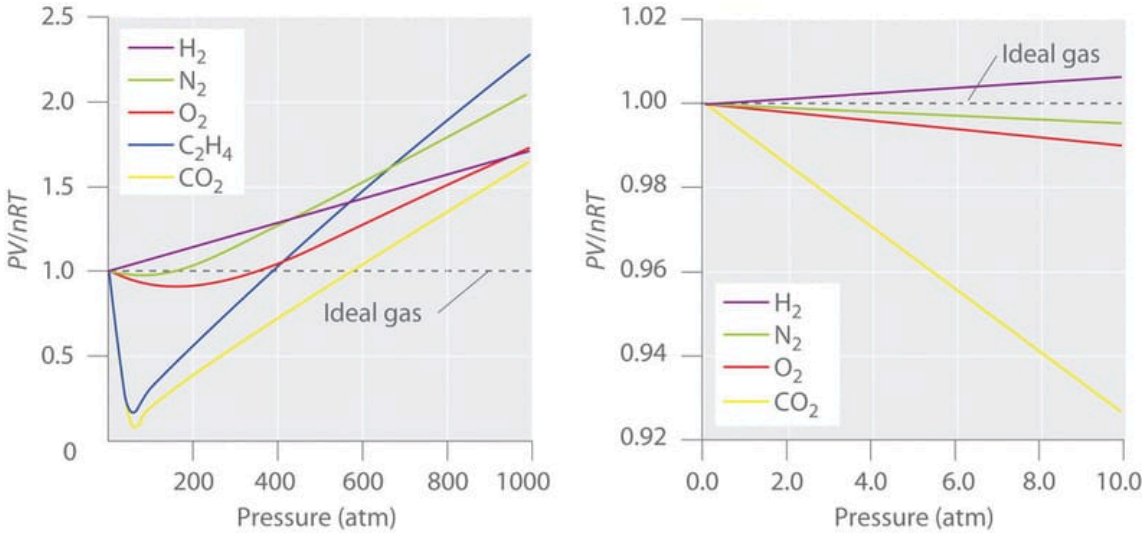
Learning Objectives

- To recognize the differences between the behavior of an ideal gas and a real gas
- To understand how molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (Figure $10.9.1a$). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (Figure $10.9.1b$).



(a) *PV/nRT* at high pressures **(b) *PV/nRT* at low pressures**

Figure $10.9.1$: Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures. (a) In these plots of *PV/nRT* versus *P* at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.

Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure $10.9.2$ for N_2. Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

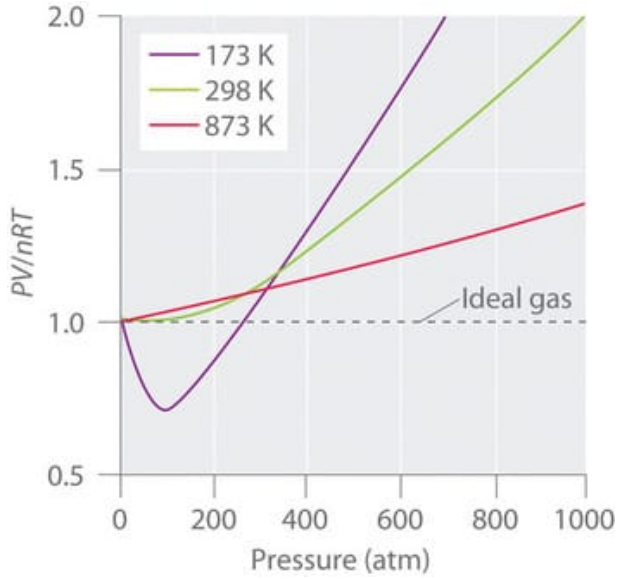


Figure 10.9.2: The Effect of Temperature on the Behavior of Real Gases. A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure 10.9.3). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of *PV/nRT* is greater than the value predicted by the ideal gas law.

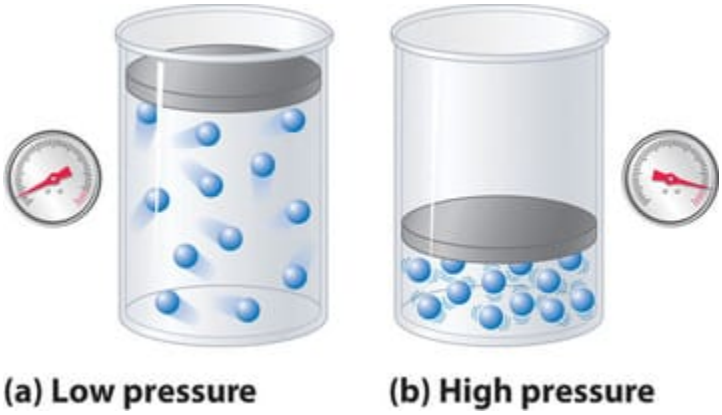


Figure 10.9.3: The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected (Figure 10.9.4). Thus as shown in Figure 10.9.2, at low temperatures, the ratio of \(PV/nRT\) is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

> Nonzero molecular volume makes the actual volume greater than predicted at high pressures; intermolecular attractions make the pressure less than predicted.

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas behavior, the so-called *van der Waals* equation,

$$\underbrace{\left(P + \frac{an^2}{V^2}\right)}_{\text{Pressure Term}} \overbrace{(V - nb)}^{\text{Pressure Term}} = nRT \tag{10.9.1}$$

a and *b* are empirical constants that are different for each gas. The values of a and b are listed in Table $10.9.1$ for several common gases.

Table $10.9.1$:: van der Waals Constants for Some Common Gases (see Table A8 for more complete list)

Gas	*a* (L^2·atm/mol^2)	*b* (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

The pressure term in Equation $10.9.1$ corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure $10.9.4$. The volume term corrects for the volume occupied by the gaseous molecules.

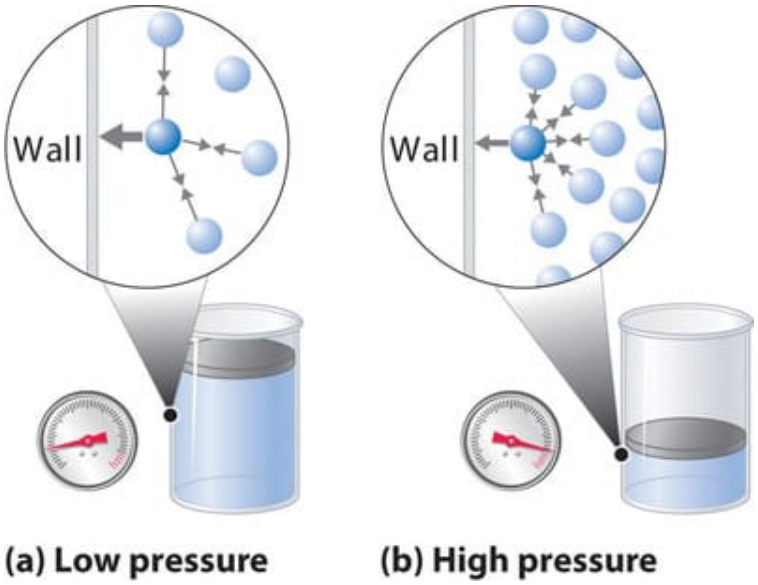


Figure 10.9.4: The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on *V* and *P*, respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the an^2/V^2 term must be added to the measured pressure to correct for these effects.

Example 10.9.1

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.00 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain *a* and *b* values for Cl_2 from Table 10.9.1. Use the van der Waals equation (10.9.1) to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$n = \frac{m}{M} \tag{10.9.2}$$

$$= \frac{500\ \text{g}}{70.906\ \text{g/mol}} \tag{10.9.3}$$

$$= 7.052\ mol$$

Using the ideal gas law and the temperature in kelvin (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} \tag{10.9.4}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L}} \tag{10.9.5}$$

$$= 43.1\ atm \tag{10.9.6}$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the *a* and *b* values for Cl_2 from Table 10.9.1. Solving for P gives

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{10.9.7}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L} - 7.052\ \text{mol} \times 0.0542 \frac{\text{L}}{\text{mol}}} - \frac{6.260 \frac{\text{L}^2\text{atm}}{\text{mol}^2} \times (7.052\ \text{mol})^2}{(4.00\ \text{L})^2} \tag{10.9.8}$$

$$= 28.2\ \text{atm} \tag{10.9.9}$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

Exercise 10.9.1

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

a. ideal gas law.
b. van der Waals equation.

Answer a available at the end of this section.

Liquefaction of Gases

Liquefaction of gases is the condensation of gases into a liquid form, which is neither anticipated nor explained by the kinetic molecular theory of gases. Both the theory and the ideal gas law predict that gases compressed to very high pressures and cooled to very low temperatures should still behave like gases, albeit cold, dense ones. As gases are compressed and cooled, however, they invariably condense to form liquids, although very low temperatures are needed to liquefy light elements such as helium (for He, 4.2 K at 1 atm pressure).

Liquefaction can be viewed as an extreme deviation from ideal gas behavior. It occurs when the molecules of a gas are cooled to the point where they no longer possess sufficient kinetic energy to overcome intermolecular attractive forces. The precise combination of temperature and pressure needed to liquefy a gas depends strongly on its molar mass and structure, with heavier and more complex molecules usually liquefying at higher temperatures. In general, substances with large van der Waals a coefficients are relatively easy to liquefy because large *a* coefficients indicate relatively strong intermolecular attractive interactions. Conversely, small molecules with only light elements have small *a* coefficients, indicating weak intermolecular interactions, and they are relatively difficult to liquefy. Gas liquefaction is used on a massive scale to separate O_2, N_2, Ar, Ne, Kr, and Xe. After a sample of air is liquefied, the mixture is warmed, and the gases are separated according to their boiling points.

A large value of a in the van der Waals equation indicates the presence of relatively strong intermolecular attractive interactions.

The ultracold liquids formed from the liquefaction of gases are called cryogenic liquids, from the Greek *kryo*, meaning “cold,” and *genes*, meaning “producing.” They have applications as refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.



Figure 10.9.5: A Liquid Natural Gas Transport Ship.

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure 10.9.5). Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are liquefied forms of hydrocarbons produced from natural gas or petroleum reserves. LNG consists mostly of methane, with small amounts of heavier hydrocarbons; it is prepared by cooling natural gas to below about −162°C. It can be stored in double-walled, vacuum-insulated containers at or slightly above atmospheric pressure. Because LNG occupies only about 1/600 the volume of natural gas, it is easier and more economical to transport. LPG is typically a mixture of propane, propene, butane, and butenes and is primarily used as a fuel for home heating. It is also used as a feedstock for chemical plants and as an inexpensive and relatively nonpolluting fuel for some automobiles.

Summary

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Deviations from ideal gas behavior can be seen in plots of *PV*/*nRT* versus *P* at a given temperature; for an ideal gas, *PV*/*nRT* versus *P* = 1 under all conditions. At high pressures, most real gases exhibit larger *PV*/*nRT* values than predicted by the ideal gas law, whereas at low pressures, most real gases exhibit *PV*/*nRT* values close to those predicted by the ideal gas law. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the **van der Waals equation**, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces. If the temperature of a gas is decreased sufficiently, **liquefaction** occurs, in which the gas condenses into a liquid form. Liquefied gases have many commercial applications, including the transport of large amounts of gases in small volumes and the uses of ultracold **cryogenic liquids**.

Answers

Exercise 10.9.1

77 atm

67 atm

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10.E: Exercises

Template:PrintMe

10.1: Characteristics of Gases

Conceptual Problems

Q10.1.1

Explain the differences between the microscopic and the macroscopic properties of matter. Is the boiling point of a compound a microscopic or macroscopic property? molecular mass? Why?

Q10.1.2

How do the microscopic properties of matter influence the macroscopic properties? Can you relate molecular mass to boiling point? Why or why not?

Q10.1.3

For a substance that has gas, liquid, and solid phases, arrange these phases in order of increasing density.

a. strength of intermolecular interactions.
b. compressibility.
c. molecular motion.
d. order in the arrangement of the molecules or atoms.

Q10.1.4

Which elements of the periodic table exist as gases at room temperature and pressure? Of these, which are diatomic molecules and which are monatomic? Which elements are liquids at room temperature and pressure? Which portion of the periodic table contains elements whose binary hydrides are most likely gases at room temperature?

10.2: Pressure

Q10.2.1

What four quantities must be known to completely describe a sample of a gas? What units are commonly used for each quantity?

Q10.2.2

If the applied force is constant, how does the pressure exerted by an object change as the area on which the force is exerted decreases? In the real world, how does this relationship apply to the ease of driving a small nail versus a large nail?

Q10.2.3

As the force on a fixed area increases, does the pressure increase or decrease? With this in mind, would you expect a heavy person to need smaller or larger snowshoes than a lighter person? Explain.

Q10.2.4

What do we mean by *barometric pressure*? Is the barometric pressure at the summit of Mt. Rainier greater than or less than the pressure in Miami, Florida? Why?

Q10.2.5

Which has the highest barometric pressure—a cave in the Himalayas, a mine in South Africa, or a beach house in Florida? Which has the lowest?

Q10.2.6

Mars has an average barometric pressure of 0.007 atm. Would it be easier or harder to drink liquid from a straw on Mars than on Earth? Explain your answer.

Q10.2.7

Is the pressure exerted by a 1.0 kg mass on a 2.0 m^2 area greater than or less than the pressure exerted by a 1.0 kg mass on a 1.0 m^2 area? What is the difference, if any, between the pressure of the atmosphere exerted on a 1.0 m^2 piston and a 2.0 m^2 piston?

Q10.2.8

If you used water in a barometer instead of mercury, what would be the major difference in the instrument?

Numerical Problems

Q10.2.9

Calculate the pressure in pascals and in atmospheres exerted by a carton of milk that weighs 1.5 kg and has a base of 7.0 cm × 7.0 cm. If the carton were lying on its side (height = 25 cm), would it exert more or less pressure? Explain your reasoning.

Q10.2.10

If barometric pressure at sea level is 1.0×10^5 Pa, what is the mass of air in kilograms above a 1.0 cm^2 area of your skin as you lie on the beach? If barometric pressure is 8.2×10^4 Pa on a mountaintop, what is the mass of air in kilograms above a 4.0 cm^2 patch of skin?

Q10.2.11

Complete the following table:

atm	kPa	mmHg	torr
1.40			
		723	
	43.2		

Q10.2.12

The SI unit of pressure is the pascal, which is equal to 1 N/m^2. Show how the product of the mass of an object and the acceleration due to gravity result in a force that, when exerted on a given area, leads to a pressure in the correct SI units. What mass in kilograms applied to a 1.0 cm^2 area is required to produce a pressure of

a. 1.0 atm?
b. 1.0 torr?
c. 1 mmHg?
d. 1 kPa?

Q10.2.13

If you constructed a manometer to measure gas pressures over the range 0.60–1.40 atm using the liquids given in the following table, how tall a column would you need for each liquid? The density of mercury is 13.5 g/cm^3. Based on your results, explain why mercury is still used in barometers, despite its toxicity.

	Liquid Density (20°C)	Column Height (m)
isopropanol	0.785	
coconut oil	0.924	
glycerine	1.259	

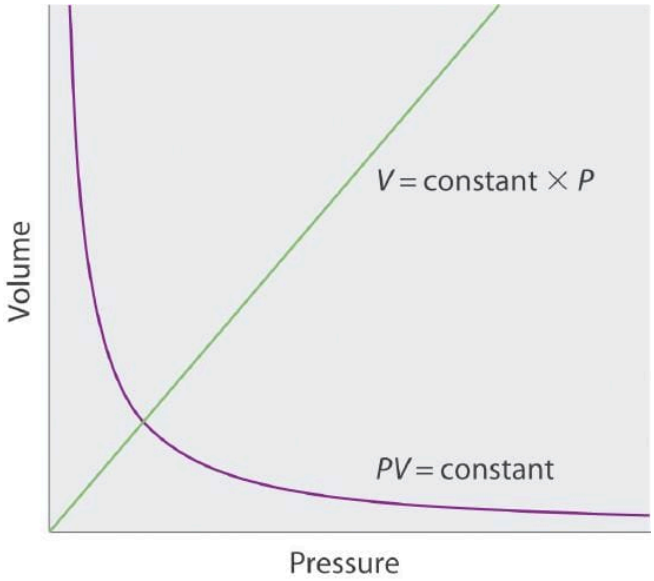
10.3: The Gas Laws

Conceptual Problems

Q10.3.1

Sketch a graph of the volume of a gas versus the pressure on the gas. What would the graph of V versus P look like if volume was directly proportional to pressure?

S10.3.1



Q10.3.2

What properties of a gas are described by Boyle's law, Charles's law, and Avogadro's law? In each law, what quantities are held constant? Why does the constant in Boyle's law depend on the amount of gas used and the temperature at which the experiments are carried out?

Q10.3.3

Use Charles's law to explain why cooler air sinks.

Q10.3.4

Use Boyle's law to explain why it is dangerous to heat even a small quantity of water in a sealed container.

Numerical Problems

Q10.3.5

A 1.00 mol sample of gas at 25°C and 1.0 atm has an initial volume of 22.4 L. Calculate the results of each change, assuming all the other conditions remain constant.

a. The pressure is changed to 85.7 mmHg. How many milliliters does the gas occupy?
b. The volume is reduced to 275 mL. What is the pressure in millimeters of mercury?
c. The pressure is increased to 25.3 atm. What is the temperature in degrees Celsius?
d. The sample is heated to 30°C. What is the volume in liters?
e. The sample is compressed to 1255 mL, and the pressure is increased to 2555 torr. What is the temperature of the gas in kelvins?

S10.3.5

a. 1.99×10^5 mL
b. 6.19×10^4 mmHg
c. 7270°C
d. 22.8 L
e. 51.4 K

Q10.3.6

A 1.00 mol sample of gas is at 300 K and 4.11 atm. What is the volume of the gas under these conditions? The sample is compressed to 6.0 atm at constant temperature, giving a volume of 3.99 L. Is this result consistent with Boyle's law?

10.4: The Ideal Gas Equation

Conceptual Problems

Q10.4.1

For an ideal gas, is volume directly proportional or inversely proportional to temperature? What is the volume of an ideal gas at absolute zero?

Q10.4.2

What is meant by STP? If a gas is at STP, what further information is required to completely describe the state of the gas?

Q10.4.3

For a given amount of a gas, the volume, temperature, and pressure under any one set of conditions are related to the volume, the temperature, and the pressure under any other set of conditions by the equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{10.E.1}$$

Q10.4.4

Derive this equation from the ideal gas law. At constant temperature, this equation reduces to one of the gas laws discussed previosuly; which one? At constant pressure, this equation reduces to one of the laws discussed in Section 10.3"; which one?

Q10.4.5

Predict the effect of each change on one variable if the other variables are held constant.

a. If the number of moles of gas increases, what is the effect on the temperature of the gas?
b. If the temperature of a gas decreases, what is the effect on the pressure of the gas?
c. If the volume of a gas increases, what is the effect on the temperature of the gas?
d. If the pressure of a gas increases, what is the effect on the number of moles of the gas?

Q10.4.6

What would the ideal gas law be if the following were true?

a. volume were proportional to pressure
b. temperature were proportional to amount
c. pressure were inversely proportional to temperature
d. volume were inversely proportional to temperature
e. both pressure and volume were inversely proportional to temperature

Given the following initial and final values, what additional information is needed to solve the problem using the ideal gas law?

Given	Solve for
V_1, T_1, T_2, n_1	n_2
P_1, P_2, T_2, n_2	n_1
T_1, T_2	V_2
P_1, n_1	P_2

Q10.4.7

Given the following information and using the ideal gas law, what equation would you use to solve the problem?

Given	Solve for
P_1, P_2, T_1	T_2
V_1, n_1, n_2	V_2

Given	Solve for
T_1, T_2, V_1, V_2, n_2	n_1

Q10.4.8

Using the ideal gas law as a starting point, derive the relationship between the density of a gas and its molar mass. Which would you expect to be denser—nitrogen or oxygen? Why does radon gas accumulate in basements and mine shafts?

Q10.4.9

Use the ideal gas law to derive an equation that relates the remaining variables for a sample of an ideal gas if the following are held constant.

a. amount and volume
b. pressure and amount
c. temperature and volume
d. temperature and amount
e. pressure and temperature

S10.4.9

a. P/T = constant
b. V/T = constant (Charles' law)
c. P/n = constant
d. PV = constant (Boyle's law)
e. V/n = constant (Avogadro's law)

Q10.4.10

Tennis balls that are made for Denver, Colorado, feel soft and do not bounce well at lower altitudes. Use the ideal gas law to explain this observation. Will a tennis ball designed to be used at sea level be harder or softer and bounce better or worse at higher altitudes?

Numerical Problems

Q10.4.11

Calculate the number of moles in each sample at STP.

a. 1580 mL of NO_2
b. 847 cm^3 of HCl
c. 4.792 L of H_2
d. a 15.0 cm × 6.7 cm × 7.5 cm container of ethane

S10.4.11

a. 7.05×10^{-2} mol
b. 3.78×10^{-2} mol
c. 0.2138 mol
d. 3.4×10^{-2} mol

Q10.4.12

Calculate the number of moles in each sample at STP.

a. 2200 cm^3 of CO_2
b. 1200 cm^3 of N_2
c. 3800 mL of SO_2
d. 13.75 L of NH_3

Q10.4.13

Calculate the mass of each sample at STP.

a. 36 mL of HI
b. 550 L of H_2S
c. 1380 cm^3 of CH_4

S10.4.13

a. 0.21 g HI;
b. 840 g H_2S;
c. 0.988 g CH_4

Q10.4.14

Calculate the mass of each sample at STP.

a. 3.2 L of N_2O
b. 65 cm^3 of Cl_2
c. 3600 mL of HBr

Q10.4.15

Calculate the volume in liters of each sample at STP.

a. 1.68 g of Kr
b. 2.97 kg of propane (C_3H_8)
c. 0.643 mg of $(CH_3)_2O$

S10.4.15

a. 0.449 L Kr
b. 1510 L C_3H_8
c. 3.13×10^{-4} L $(CH_3)_2O$

Q10.4.16

Calculate the volume in liters of each sample at STP.

a. 3.2 g of Xe
b. 465 mg of CS_2
c. 5.34 kg of acetylene (C_2H_2)

Q10.4.17

Calculate the volume of each gas at STP.

a. 1.7 L at 28°C and 96.4 kPa
b. 38.0 mL at 17°C and 103.4 torr
c. 650 mL at −15°C and 723 mmHg

Q10.4.18

Calculate the volume of each gas at STP.

a. 2.30 L at 23°C and 740 mmHg
b. 320 mL at 13°C and 97.2 kPa
c. 100.5 mL at 35°C and 1.4 atm

S10.4.18

a. 1.5 L
b. 4.87 mL
c. 650 mL

Q10.4.19

A 8.60 L tank of nitrogen gas at a pressure of 455 mmHg is connected to an empty tank with a volume of 5.35 L. What is the final pressure in the system after the valve connecting the two tanks is opened? Assume that the temperature is constant.

S10.4.19

281 mmHg

Q10.4.20

At constant temperature, what pressure in atmospheres is needed to compress 14.2 L of gas initially at 25.2 atm to a volume of 12.4 L? What pressure is needed to compress 27.8 L of gas to 20.6 L under similar conditions?

Q10.4.21

One method for preparing hydrogen gas is to pass HCl gas over hot aluminum; the other product of the reaction is $AlCl_3$. If you wanted to use this reaction to fill a balloon with a volume of 28,500 L at sea level and a temperature of 78°F, what mass of aluminum would you need? What volume of HCl at STP would you need?

S10.4.21

20.9 kg Al, 5.20×10^4 L HCl

Q10.4.21

An 3.50 g sample of acetylene is burned in excess oxygen according to the following reaction:

$$2\,C_2H_2\,(g) + 5\,O_2\,(g) \longrightarrow 4\,CO_2\,(g) + 2\,H_2O\,(l) \tag{10.E.2}$$

At STP, what volume of CO_2(g) is produced?

Q10.4.22

Calculate the density of ethylene (C_2H_4) under each set of conditions.

a. 7.8 g at 0.89 atm and 26°C
b. 6.3 mol at 102.6 kPa and 38°C
c. 9.8 g at 3.1 atm and –45°C

S10.4.22

a. 1.0 g/L
b. 1.1 g/L
c. 4.6 g/L

Q10.4.23

Determine the density of O_2 under each set of conditions.

a. 42 g at 1.1 atm and 25°C
b. 0.87 mol at 820 mmHg and 45°C
c. 16.7 g at 2.4 atm and 67°C

Q10.4.24

At 140°C, the pressure of a diatomic gas in a 3.0 L flask is 635 kPa. The mass of the gas is 88.7 g. What is the most likely identity of the gas?

Q10.4.25

What volume must a balloon have to hold 6.20 kg of H_2 for an ascent from sea level to an elevation of 20,320 ft, where the temperature is –37°C and the pressure is 369 mmHg?

Q10.4.26

What must be the volume of a balloon that can hold 313.0 g of helium gas and ascend from sea level to an elevation of 1.5 km, where the temperature is 10.0°C and the pressure is 635.4 mmHg?

S10.4.26

2174 L

Q10.4.27

A typical automobile tire is inflated to a pressure of 28.0 lb/in.^{2} Assume that the tire is inflated when the air temperature is 20°C; the car is then driven at high speeds, which increases the temperature of the tire to 43°C. What is the pressure in the tire? If the volume of the tire had increased by 8% at the higher temperature, what would the pressure be?

Q10.4.28

The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at 20°C and 0.997 atm, how many moles of air does a person inhale each day? If the density of air is 1.19 kg/m^3, what is the average molecular mass of air?

Q10.4.29

Kerosene has a self-ignition temperature of 255°C. It is a common accelerant used by arsonists, but its presence is easily detected in fire debris by a variety of methods. If a 1.0 L glass bottle containing a mixture of air and kerosene vapor at an initial pressure of 1 atm and an initial temperature of 23°C is pressurized, at what pressure would the kerosene vapor ignite?

10.5: Further Applications of the Ideal-Gas Equations

Conceptual Problems

Q10.5.1

Why are so many industrially important reactions carried out in the gas phase?

Q10.5.2

The volume of gas produced during a chemical reaction can be measured by collecting the gas in an inverted container filled with water. The gas forces water out of the container, and the volume of liquid displaced is a measure of the volume of gas. What additional information must be considered to determine the number of moles of gas produced? The volume of some gases cannot be measured using this method. What property of a gas precludes the use of this method?

Q10.5.3

Equal masses of two solid compounds (A and B) are placed in separate sealed flasks filled with air at 1 atm and heated to 50°C for 10 hours. After cooling to room temperature, the pressure in the flask containing A was 1.5 atm. In contrast, the pressure in the flask containing B was 0.87 atm. Suggest an explanation for these observations. Would the masses of samples A and B still be equal after the experiment? Why or why not?

Numerical Problems

Q10.5.4

Balance each chemical equation and then determine the volume of the indicated reactant at STP that is required for complete reaction. Assuming complete reaction, what is the volume of the products?

a. $SO_2(g) + O_2(g) \rightarrow SO_3(g)$ given 2.4 mol of O_2
b. $H_2(g) + Cl_2(g) \rightarrow HCl(g)$ given 0.78 g of H_2
c. $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$ given 1.91 mol of O_2

Q10.5.5

During the smelting of iron, carbon reacts with oxygen to produce carbon monoxide, which then reacts with iron(III) oxide to produce iron metal and carbon dioxide. If 1.82 L of CO_2 at STP is produced,

a. what mass of CO is consumed?
b. what volume of CO at STP is consumed?
c. how much O_2 (in liters) at STP is used?
d. what mass of carbon is consumed?
e. how much iron metal (in grams) is produced?

Q10.5.6

Complete decomposition of a sample of potassium chlorate produced 1.34 g of potassium chloride and oxygen gas.

a. What is the mass of $KClO_3$ in the original sample?
b. What mass of oxygen is produced?
c. What is the volume of oxygen produced at STP?

S10.5.6

a. 2.20 g $KClO_3$
b. 0.863 g O_2
c. 604 mL O_2

Q10.5.7

The combustion of a 100.0 mg sample of an herbicide in excess oxygen produced 83.16 mL of CO_2 and 72.9 mL of H_2O vapor at STP. A separate analysis showed that the sample contained 16.44 mg of chlorine. If the sample is known to contain only C, H, Cl, and N, determine the percent composition and the empirical formula of the herbicide.

Q10.5.8

The combustion of a 300.0 mg sample of an antidepressant in excess oxygen produced 326 mL of CO_2 and 164 mL of H_2O vapor at STP. A separate analysis showed that the sample contained 23.28% oxygen. If the sample is known to contain only C, H, O, and N, determine the percent composition and the empirical formula of the antidepressant.

S10.5.8

Percent composition: 58.3% C, 4.93% H, 23.28% O, and 13.5% N; empirical formula: $C_{10}H_{10}O_3N_2$

10.6: Gas Mixtures and Partial Pressures

Conceptual Problems

Q10.6.1

Dalton's law of partial pressures makes one key assumption about the nature of the intermolecular interactions in a mixture of gases. What is it?

Q10.6.2

What is the relationship between the partial pressure of a gas and its mole fraction in a mixture?

Numerical Problems

Q10.6.3

What is the partial pressure of each gas if the following amounts of substances are placed in a 25.0 L container at 25°C? What is the total pressure of each mixture?

a. 1.570 mol of CH_4 and 0.870 mol of CO_2

b. 2.63 g of CO and 1.24 g of NO_2
c. 1.78 kg of CH_3Cl and 0.92 kg of SO_2

Q10.6.4

What is the partial pressure of each gas in the following 3.0 L mixtures at 37°C as well as the total pressure?

a. 0.128 mol of SO_2 and 0.098 mol of methane (CH_4)
b. 3.40 g of acetylene (C_2H_2) and 1.54 g of He
c. 0.267 g of NO, 4.3 g of Ar, and 0.872 g of SO_2

Q10.6.5

In a mixture of helium, oxygen, and methane in a 2.00 L container, the partial pressures of He and O_2 are 13.6 kPa and 29.2 kPa, respectively, and the total pressure inside the container is 95.4 kPa. What is the partial pressure of methane? If the methane is ignited to initiate its combustion with oxygen and the system is then cooled to the original temperature of 30°C, what is the final pressure inside the container (in kilopascals)?

S10.6.5

52.6 kPa, 66.2 kPa

Q10.6.6

A 2.00 L flask originally contains 1.00 g of ethane (C_2H_6) and 32.0 g of oxygen at 21°C. During ignition, the ethane reacts completely with oxygen to produce CO_2 and water vapor, and the temperature of the flask increases to 200°C. Determine the total pressure and the partial pressure of each gas before and after the reaction.

Q10.6.7

If a 20.0 L cylinder at 19°C is charged with 5.0 g each of sulfur dioxide and oxygen, what is the partial pressure of each gas? The sulfur dioxide is ignited in the oxygen to produce sulfur trioxide gas, and the mixture is allowed to cool to 19°C at constant pressure. What is the final volume of the cylinder? What is the partial pressure of each gas in the piston?

Q10.6.8

The highest point on the continent of Europe is Mt. Elbrus in Russia, with an elevation of 18,476 ft. The highest point on the continent of South America is Mt. Aconcagua in Argentina, with an elevation of 22,841 ft.

a. The following table shows the variation of atmospheric pressure with elevation. Use the data in the table to construct a plot of pressure versus elevation.

Elevation (km)	Pressure in Summer (mmHg)	Pressure in Winter (mmHg)
0.0	760.0	760.0
1.0	674.8	670.6
1.5	635.4	629.6
2.0	598.0	590.8
3.0	528.9	519.7
5.0	410.6	398.7
7.0	314.9	301.6

Elevation (km)	Pressure in Summer (mmHg)	Pressure in Winter (mmHg)
9.0	237.8	224.1

b. Use your graph to estimate the pressures in millimeters of mercury during the summer and the winter at the top of both mountains in both atmospheres and kilopascals.
c. Given that air is 20.95% O_2 by volume, what is the partial pressure of oxygen in atmospheres during the summer at each location?

10.7: Kinetic-Molecular Theory

10.8: Molecular Effusion and Diffusion

Conceptual Problems

Q10.8.1

Which of the following processes represents effusion, and which represents diffusion?

a. helium escaping from a hole in a balloon
b. vapor escaping from the surface of a liquid
c. gas escaping through a membrane

Q10.8.2

Which postulate of the kinetic molecular theory of gases most readily explains the observation that a helium-filled balloon is round?

Q10.8.3

Why is it relatively easy to compress a gas? How does the compressibility of a gas compare with that of a liquid? A solid? Why? Which of the postulates of the kinetic molecular theory of gases most readily explains these observations?

Q10.8.4

What happens to the average kinetic energy of a gas if the rms speed of its particles increases by a factor of 2? How is the rms speed different from the average speed?

Q10.8.5

Which gas—radon or helium—has a higher average kinetic energy at 100°C? Which has a higher average speed? Why? Which postulate of the kinetic molecular theory of gases most readily supports your answer?

Q10.8.6

What is the relationship between the average speed of a gas particle and the temperature of the gas? What happens to the distribution of molecular speeds if the temperature of a gas is increased? Decreased?

Q10.8.7

Qualitatively explain the relationship between the number of collisions of gas particles with the walls of a container and the

pressure of a gas. How does increasing the temperature affect the number of collisions?

Q10.8.8

What happens to the average kinetic energy of a gas at constant temperature if the

a. volume of the gas is increased?
b. pressure of the gas is increased?

Q10.8.9

What happens to the density of a gas at constant temperature if the

a. volume of the gas is increased?
b. pressure of the gas is increased?

Q10.8.10

Use the kinetic molecular theory of gases to describe how a decrease in volume produces an increase in pressure at constant temperature. Similarly, explain how a decrease in temperature leads to a decrease in volume at constant pressure.

Q10.8.11

Graham's law is valid only if the two gases are at the same temperature. Why?

Q10.8.12

If we lived in a helium atmosphere rather than in air, would we detect odors more or less rapidly than we do now? Explain your reasoning. Would we detect odors more or less rapidly at sea level or at high altitude? Why?

Numerical Problems

Q10.8.13

At a given temperature, what is the ratio of the rms speed of the atoms of Ar gas to the rms speed of molecules of H_2 gas?

S10.8.13

At any temperature, the rms speed of hydrogen is 4.45 times that of argon.

Q10.8.14

At a given temperature, what is the ratio of the rms speed of molecules of CO gas to the rms speed of molecules of H_2S gas?

Q10.8.15

What is the ratio of the rms speeds of argon and oxygen at any temperature? Which diffuses more rapidly?

Q10.8.16

What is the ratio of the rms speeds of Kr and NO at any temperature? Which diffuses more rapidly?

Q10.8.17

Deuterium (D) and tritium (T) are heavy isotopes of hydrogen. Tritium has an atomic mass of 3.016 amu and has a natural abundance of 0.000138%. The effusion of hydrogen gas (containing a mixture of H_2, HD, and HT molecules) through a porous membrane can be used to obtain samples of hydrogen that are enriched in tritium. How many membrane passes are necessary to give a sample of hydrogen gas in which 1% of the hydrogen molecules are HT?

Q10.8.18

Samples of HBr gas and NH_3 gas are placed at opposite ends of a 1 m tube. If the two gases are allowed to diffuse through the tube toward one another, at what distance from each end of the tube will the gases meet and form solid NH_4Br?

10.9: Real Gases: Deviations from Ideal Behavior

Conceptual Problems

Q10.9.1

What factors cause deviations from ideal gas behavior? Use a sketch to explain your answer based on interactions at the molecular level.

Q10.9.2

Explain the effect of nonzero atomic volume on the ideal gas law at high pressure. Draw a typical graph of volume versus 1/*P* for an ideal gas and a real gas.

Q10.9.3

For an ideal gas, the product of pressure and volume should be constant, regardless of the pressure. Experimental data for methane, however, show that the value of *PV* decreases significantly over the pressure range 0 to 120 atm at 0°C. The decrease in *PV* over the same pressure range is much smaller at 100°C. Explain why *PV* decreases with increasing temperature. Why is the decrease less significant at higher temperatures.

Q10.9.4

What is the effect of intermolecular forces on the liquefaction of a gas? At constant pressure and volume, does it become easier or harder to liquefy a gas as its temperature increases? Explain your reasoning. What is the effect of increasing the pressure on the liquefaction temperature?

Q10.9.5

Describe qualitatively what *a* and *b*, the two empirical constants in the van der Waals equation, represent.

Q10.9.6

In the van der Waals equation, why is the term that corrects for volume negative and the term that corrects for pressure positive? Why is *n*/*V* squared?

Q10.9.7

Liquefaction of a gas depends strongly on two factors. What are they? As temperature is decreased, which gas will liquefy

first—ammonia, methane, or carbon monoxide? Why?

Q10.9.8

What is a cryogenic liquid? Describe three uses of cryogenic liquids.

Q10.9.9

Air consists primarily of O_2, N_2, Ar, Ne, Kr, and Xe. Use the concepts discussed in this chapter to propose two methods by which air can be separated into its components. Which component of air will be isolated first?

Q10.9.10

How can gas liquefaction facilitate the storage and transport of fossil fuels? What are the potential drawbacks to these methods?

Numerical Problems

Q10.9.11

The van der Waals constants for xenon are a = 4.19 $(L^2 \cdot atm)/mol^2$ and b = 0.0510 L/mol. If a 0.250 mol sample of xenon in a container with a volume of 3.65 L is cooled to −90°C, what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?

Q10.9.12

The van der Waals constants for water vapor are a = 5.46 $(L^2 \cdot atm)/mol^2$ and b = 0.0305 L/mol. If a 20.0 g sample of water in a container with a volume of 5.0 L is heated to 120°C, what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?

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10.S: Gases (Summary)

10.1: Characteristics of Gases

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2, O_2).

- Gases expand spontaneously to fill containers in which they are held, equaling their volume. Consequently, they are highly compressible.
- Gases form homogeneous mixtures with each other *regardless* of the identities or relative proportions of the component gases
- The characteristic properties of gases arise because the individual molecules are relatively far apart, hence, acting largely as though they were alone.

10.2: Pressure

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. Four quantities must be known for a complete physical description of a sample of a gas: temperature, volume, amount, and pressure. Pressure is force per unit area of surface; the SI unit for pressure is the pascal (Pa), defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area.

- Pressure, *P*, is the Force, *F*, that acts on a given Area, *A*:

$$P = F/A$$

Atmospheric Pressure and the Barometer

- The force, *F*, exerted by any object is the product of its mass, *m*, times its acceleration, *a*: *F* = *ma*
- SI unit for force is kg-m/s^2 and is called the *Newton* (N)
- SI unit of pressure is N/m^2, called a Pascal
- **Standard atmospheric pressure**: defined as 760 torr (760 mm Hg), or, in SI units, 101.325 kPa
- **Atmosphere**: unit of pressure equal to 760 torr; 1 atm = 101.325 kPa

10.3: The Gas Laws

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to pressure (Boyle's law), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature at constant pressure (Charles's law), and Avogadro showed that the volume of a gas is directly proportional to the number of moles of gas (Avogadro's law).

The Pressure-Volume Relationship: Boyle's Law

- Boyle's law states that the volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the pressure. When two measurements are inversely proportional, one gets smaller as the other one gets larger.

$$PV = constant$$

where P = pressure, V = volume

The Temperature-Volume Relationship: Charles's Law

- **Charles's law**: states that the volume of a fixed amount of gas maintained at constant pressure is directly proportional to its

absolute temperature. Thus, as the pressure gets higher, so does the temperature.

$$\frac{V}{T} = constant$$

where V = volume, T = Temperature

The Quantity-Volume Relationship: Avogadro's Law

- **Law of combining volumes**: at a given pressure and temperature, the volumes of gases that react with one another are in the ratios of small whole numbers. (ie: $2H_2 + O_2 = 2H_2O$)
- **Avogadro's hypothesis**: equal volumes of gases at the same temperature and pressure contain equal number of molecules
- **Avogadro's law**: The volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas

$$V = constant \times n$$

where V = volume, *n* = number of moles

10.4: The Ideal Gas Equation

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the ideal gas law, PV = nRT. The proportionality constant, R, is called the gas constant. The ideal gas law describes the behavior of an ideal gas, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. Standard temperature and pressure (STP) is 0°C and 1 atm.

Ideal-gas equation

$$PV = nRT$$

where P = pressure, V = volume, n = number of moles, R = gas constant, T = Temperature (always expressed on absolute-temperature scale, usually Kelvin)

The *Gas constant* (R) is the constant of proportionality in the ideal-gas equation. Some values of R are given below

Some values of R

Units	Numerical value
L-atm/mol-K	0.08206
Cal/mol-K	1.987
J/mol-K	8.314
M^3-Pa/mol-K	8.314
L-torr/mol-K	62.36

Standard temperature and pressure (STP): 0°C and 1 atm. 1 mol of gas at STP has a volume of 22.41 L (*molar volume*)

10.5: Further Applications of the Ideal-Gas Equations

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can be calculated from the volume of water displaced.

Density of a gas (*\rho\) = density, M = molar mass):

\[\rho = \dfrac{PM}{ RT} \nonumber \]

Molar mass of a gas:

$$M = \frac{\rho RT}{P}$$

10.6: Gas Mixtures and Partial Pressures

The pressure exerted by each gas in a gas mixture is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (Dalton's law of partial pressures). The amount of gas in a mixture may be described by its partial pressure or its mole fraction. In a mixture, the partial pressure of each gas is the product of the total pressure and the mole fraction.

- **Partial pressure**: the pressure exerted by a particular gas in a mixture
- **Dalton's law of partial pressures**: law stating that the total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone

The total pressure at constant temperature and volume is determined by the total number of moles of gas present, whether that total represents just one substance or a mixture

Partial Pressures and Mole Fractions

- **Mole fraction**: the ratio of the number of one component of a mixture to the total moles of all components; abbreviated χ, with a subscript to identify the components.

The partial pressure of a gas in a mixture is its mole fraction times the total pressure

10.7: Kinetic-Molecular Theory

The behavior of ideal gases is explained by the kinetic molecular theory of gases. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same root mean square speed. The actual values of speed and kinetic energy are not the same for all gas particles.

Kinetic-molecular theory: set of assumptions about the nature of gases. These assumptions, when translated into mathematical form, yield the ideal-gas equation

1. Gases consist of large numbers of molecules that are in continuous, random motion
2. The volume of all the molecules of the gas is negligible compared to the total volume in which the gas is contained
3. Attractive and repulsive forces between gas molecules are negligible
4. Energy can be transferred between molecules during collisions, but the *average* kinetic energy of the molecules does *not* change with time, as long as the temperature of the gas remains constant
5. The average kinetic energy of the molecules is proportional to absolute temperature. At any given temperature, the molecules of all gases have the same average kinetic energy

The pressure of a gas is caused by collisions of molecules with the walls of the container. The magnitude of the pressure is determined by how often and how "hard" the molecules strike the walls.

If two different gases are at the same temperature, they have the same average kinetic energy. If the temperature of a gas is doubled, its kinetic energy also doubles. Hence, molecular motion increases with increasing temperature.

- **Root-mean-square (rms) speed**: the square root of the squared speeds of the gas molecules in a gas sample. This quantity is the speed of a molecule possessing average kinetic energy.

The rms speed is important because the average kinetic energy of the gas molecules, ε, is related directly to u^2:

$$\varepsilon = \frac{1}{2}mu^2$$

where m is the mass of the molecule

Because mass doesn't change with temperature, the rms speed (and also the average speed) of molecules must increase as temperature increases

Applications to the Gas Laws

1. *Effect of a volume increase at constant temperature*: If the volume is increased, the molecules must move a longer distance between collisions. Consequently, there are fewer collisions per unit time with the container walls, and pressure decreases.
2. *Effect of a temperature increase at constant volume*: An increases in temperature means an increase in the average kinetic energy of the molecules. If there is no change in volume, there will be more collisions with the walls per unit time. Furthermore, the molecules strike harder, hence explaining how the observed pressure increases.

10.8: Molecular Effusion and Diffusion

Diffusion is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, effusion is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (Graham's law), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases.

A gas composed of light gas particles will have the same average kinetic energy as one composed of much heavier particles, provided that the two gases are at the same temperature. The mass, m, of the particles in the lighter gas is smaller that that in the heavier gas. Consequently, the particles of the lighter gas must have a higher rms speed, u, than the heavier one:

$$u = \sqrt{\frac{3RT}{M}}$$

Since M is in the denominator, the less massive the gas molecules, the higher the rms speed

- **Effusion**: the escape of a gas through an orifice or hole. The rate of effusion depends on the molecular mass of the gas.
- **Diffusion**: the spreading of one substance through a space or through another substance

Graham's Law of Effusion

- **Graham's law**: law stating that the rate of effusion of a gas is inversely proportional to the square root of its molecular weight

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

where r is the rate of effusion

- The rate of effusion is also directly proportional to the rms speed of the molecules. This is because the only way for the molecule to escape is to "collide" with the opening. Hence, the faster the molecules are moving, the greater the likelihood that a molecule will hit the opening and effuse.

Diffusion and Mean Free Path

- Diffusion, like effusion, is faster for light molecules than for heavy ones. The diffusion of gases is much slower than molecular speeds because of molecular collisions. Because of these collisions, the direction of motion of a gas molecule is constantly changing, making this a slow process.
- **Mean free path**: average distance traveled by a molecule between collisions. The higher the density of a gas, the smaller the mean free path

10.9: Real Gases - Deviations from Ideal Behavior

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the van der Waals equation, which includes empirical constants to correct for the actual volume of the gaseous molecules and

quantify the reduction in pressure due to intermolecular attractive forces.

The ideal gas equation may be rearranged as follows to understand deviations from ideal-gas behavior:

$$\frac{PV}{RT} = n$$

- For a mole of ideal gas (n = 1), the quantity PV / RT = 1 at all pressures. However, real gases do not behave in such a way. At high pressures, the deviation is very high, however it is less with lower pressures. In general, the deviations from idea behavior increase as temperature decreases, becoming significant near the temperature at which the gas is converted into a liquid.
- Basic assumptions in the kinetic molecular theory suggest that molecules of an ideal gas occupy no space and have no attraction for each other. *Real molecules, however, do have finite volumes, and they do attract one another*.
- Also, if the volume of the container in which the gas is contained is large, the molecules have plenty of free space, and do not take much of the container's volume itself. However, as pressure increases, the gas molecules occupy a much larger fraction of the container's volume.
- In addition, the attractive forces between molecules come into play at short distances, as when molecules are crowded together at high pressures. Because of these attractive forces, the impact of a given molecule with the wall of the container is lessened.
- Temperature determines how effective attractive forces between gas molecules are. As the gas is cooled, the average kinetic energy decreases, while intermolecular attractions remain constant.

The Van der Walls Equation

According to the ideal gas equation:

$$\underbrace{P = \frac{nRT}{V}}_{\text{ideal gas}}$$

According to Van der Waals:

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Correction for volume of molecules – Correction for molecular attractions

- The Van der Waals constant b is a measure of the actual volume occupied by a mole of gas molecules; b has units of L/mol.
- The Van der Walls constant a has units of L^2-atm/mol^2. The magnitude of a reflects how strongly the gas molecules attract each other

Van der Waals equation

$$\left[P + \left(\frac{n^2 a}{V^2}\right)\right](V - nb) = nRT$$

The Van der Waals constants a and b are different for each gas. The values of these constants generally increase with an increase in mass of the molecule and with an increase in the complexity of its structures.

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11: LIQUIDS AND INTERMOLECULAR FORCES

The physical properties of a substance depends upon its physical state. Water vapor, liquid water and ice all have the same chemical properties, but their physical properties are considerably different. In general Covalent bonds determine: molecular shape, bond energies, chemical properties, while intermolecular forces (non-covalent bonds) influence the physical properties of liquids and solids. The kinetic molecular theory of gases described in Chapter 10 gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

11.1: A Molecular Comparison of Gases, Liquids, and Solids

11.2: Intermolecular Forces

11.3: Some Properties of Liquids

11.4: Phase Changes

11.5: Vapor Pressure

11.6: Phase Diagrams

11.7: Structure of Solids

11.8: Bonding in Solids

11.E: Liquids and Intermolecular Forces (Exercises)

11.S: Liquids and Intermolecular Forces (Summary)

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11.1: A Molecular Comparison of Gases, Liquids, and Solids

Learning Objectives

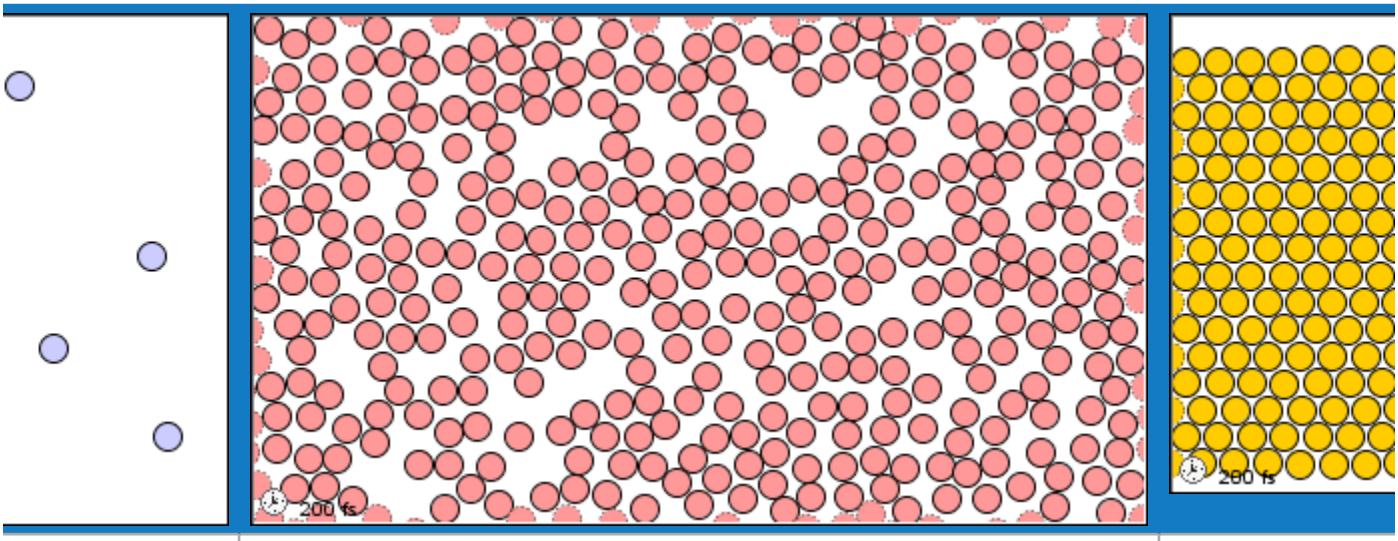
- To be familiar with the kinetic molecular description of liquids.

The *physical* properties of a substance depends upon its physical state. Water vapor, liquid water and ice all have the same *chemical* properties, but their *physical* properties are considerably different. In general *covalent bonds* determine: molecular shape, bond energies, *chemical* properties, while *intermolecular forces* (non-covalent bonds) influence the *physical* properties of liquids and solids. The kinetic molecular theory of gases gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.



Figure 11.1.1: The three common states of matter. From the left, they are solid, liquid, and gas, represented by an ice sculpture, a drop of water, and the air around clouds, respectively. Images used with permission from Wikipedia.

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance. The intermolecular forces are attractive forces that try to draw the particles together (Figure 11.1.2). A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces.



(b) as a liquid

Figure 11.1.2: Molecular level picture of gases, liquids and solids.

Below is an overview of the general properties of the three different phases of matter.

Properties of Gases

- A collection of widely separated molecules
- The kinetic energy of the molecules is greater than any attractive forces between the molecules
- The lack of any significant attractive force between molecules allows a gas to expand to fill its container
- If attractive forces become large enough, then the gases exhibit non-ideal behavior

Properties of Liquids

- The intermolecular attractive forces are strong enough to hold molecules close together
- Liquids are more dense and less compressible than gasses
- Liquids have a definite volume, independent of the size and shape of their container
- The attractive forces are ***not*** strong enough, however, to keep neighboring molecules in a fixed position and molecules are free to move past or slide over one another

Thus, liquids can be poured and assume the shape of their containers.

Properties of Solids

- The intermolecular forces between neighboring molecules are strong enough to keep them locked in position
- Solids (like liquids) are not very compressible due to the lack of space between molecules
- If the molecules in a solid adopt a highly ordered packing arrangement, the structures are said to be ***crystalline***

Due to the strong intermolecular forces between neighboring molecules, solids are rigid.

- Cooling a gas may change the state to a liquid
- Cooling a liquid may change the state to a solid
- Increasing the pressure on a gas may change the state to a liquid
- Increasing the pressure on a liquid may change the state to a solid

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 11.1.1: Video highlighting the properties for the three states of matter. Source found at www.youtube.com/watch?v=s-KvoVzukHo.

Physical Properties of Liquids

In a gas, the distance between molecules, whether monatomic or polyatomic, is very large compared with the size of the molecules; thus gases have a low density and are highly compressible. In contrast, the molecules in liquids are very close together, with essentially no empty space between them. As in gases, however, the molecules in liquids are in constant motion, and their kinetic energy (and hence their speed) depends on their temperature. We begin our discussion by examining some of the characteristic properties of liquids to see how each is consistent with a modified kinetic molecular description.

The properties of liquids can be explained using a modified version of the kinetic molecular theory of gases described previously. This model explains the higher density, greater order, and lower compressibility of liquids versus gases; the thermal expansion of liquids; why they diffuse; and why they adopt the shape (but not the volume) of their containers. A kinetic molecular description of liquids must take into account both the nonzero volumes of particles and the presence of strong intermolecular attractive forces. Solids and liquids have particles that are fairly close to one another, and are thus called "**condensed phases**" to distinguish them from gases

- **Density**: The molecules of a liquid are packed relatively close together. Consequently, liquids are much denser than gases. The density of a liquid is typically about the same as the density of the solid state of the substance. Densities of liquids are therefore more commonly measured in units of grams per cubic centimeter (g/cm^3) or grams per milliliter (g/mL) than in grams per liter (g/L), the unit commonly used for gases.
- **Molecular Order:** Liquids exhibit short-range order because strong intermolecular attractive forces cause the molecules to pack together rather tightly. Because of their higher kinetic energy compared to the molecules in a solid, however, the molecules in a liquid move rapidly with respect to one another. Thus unlike the ions in the ionic solids, the molecules in liquids are not arranged in a repeating three-dimensional array. Unlike the molecules in gases, however, the arrangement of the molecules in a liquid is not completely random.
- **Compressibility**: Liquids have so little empty space between their component molecules that they cannot be readily compressed. Compression would force the atoms on adjacent molecules to occupy the same region of space.
- **Thermal Expansion**: The intermolecular forces in liquids are strong enough to keep them from expanding significantly when heated (typically only a few percent over a 100°C temperature range). Thus the volumes of liquids are somewhat fixed. Notice from Table S1 (with a shorten version in Table 11.1.1) that the density of water, for example, changes by only about 3% over a 90-degree temperature range.

Table 11.1.1: The Density of Water at Various Temperatures

T (°C)	Density (g/cm^3)
0	0.99984
30	0.99565
60	0.98320
90	0.96535

- **Diffusion**: Molecules in liquids diffuse because they are in constant motion. A molecule in a liquid cannot move far before colliding with another molecule, however, so the mean free path in liquids is very short, and the rate of diffusion is much slower than in gases.

- **Fluidity**: Liquids can flow, adjusting to the shape of their containers, because their molecules are free to move. This freedom of motion and their close spacing allow the molecules in a liquid to move rapidly into the openings left by other molecules, in turn generating more openings, and so forth (Figure 11.1.3).

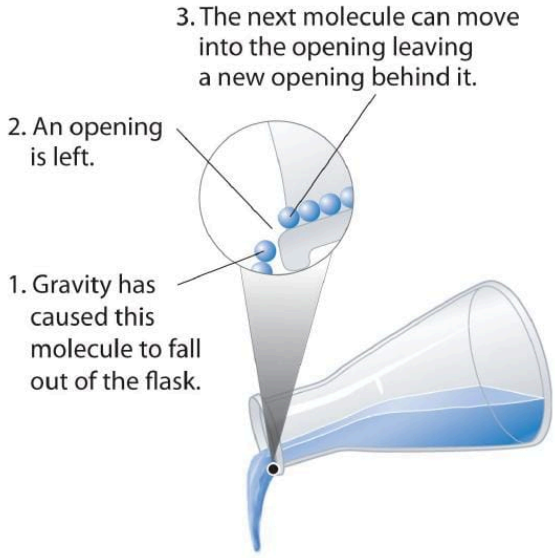


Figure 11.1.3: Why Liquids Flow. Molecules in a liquid are in constant motion. Consequently, when the flask is tilted, molecules move to the left and down due to the force of gravity, and the openings are occupied by other molecules. The result is a net flow of liquid out of the container. (CC BY-SA-NC; Anonymous vy request).

Contributors and Attributions

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11.2: Intermolecular Forces

Learning Objectives

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids.

Intermolecular forces determine bulk properties, such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures.

In this section, we explicitly consider three kinds of intermolecular interactions. There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding, and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure $11.2.1a$.

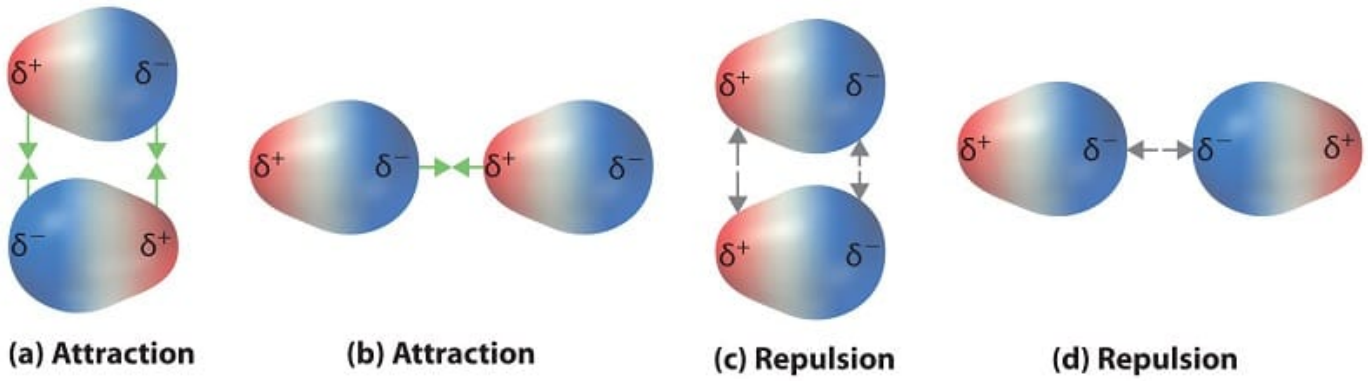


Figure 11.2.1: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions. (CC BY-SA-NC; anonymous)

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure 11.2.1*c*). Hence dipole–dipole interactions, such as those in Figure 11.2.1*b*, are *attractive intermolecular interactions*, whereas those in Figure 11.2.1*d* are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 11.2.2. On average, however, the attractive interactions dominate.

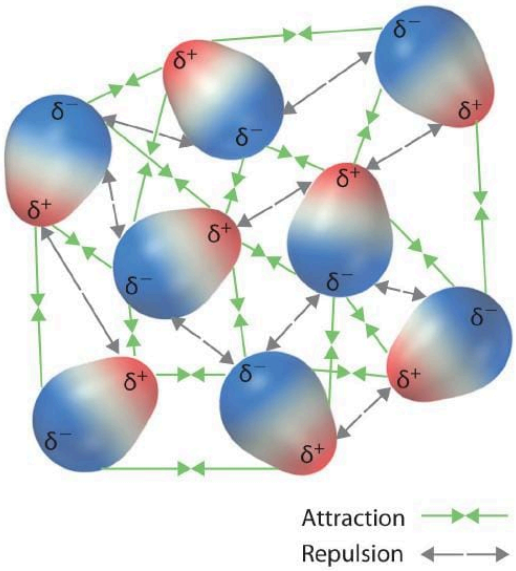


Figure 11.2.2: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules. (CC BY-SA-NC; anonymous)

The green arrows pointing towards each other represent attraction. The gray arrows pointing away from each other represent repulsion

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^3$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^3, or 8-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure. Conversely, NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 11.2.1.

Table 11.2.1: Relationships Between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.

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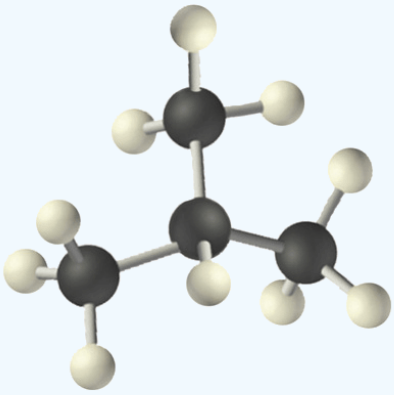
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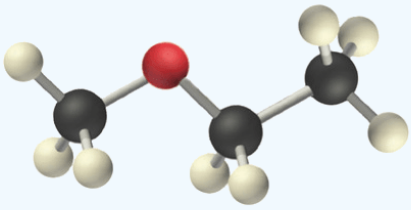
Video Discussing Dipole Intermolecular Forces. Source: Dipole Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 11.2.1

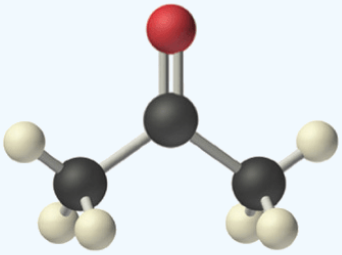
Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



2-Methylpropane



Ethyl methyl ether



Acetone

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds.

The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point.

Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point.

Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.

Thus we predict the following order of boiling points:

2-methylpropane < ethyl methyl ether < acetone

This result is in good agreement with the actual data: 2-methylpropane, boiling point = –11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise 11.2.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer available at the end of this section.

London Dispersion Forces

Thus far, we have considered only interactions between polar molecules. Other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature; why others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 11.2.2).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 11.2.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	–189.4	–185.9
Xe	131	–111.8	–108.1
N_2	28	–210	–195.8
O_2	32	–218.8	–183.0
F_2	38	–219.7	–188.1
I_2	254	113.7	184.4
CH_4	16	–182.5	–161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed

around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 11.2.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

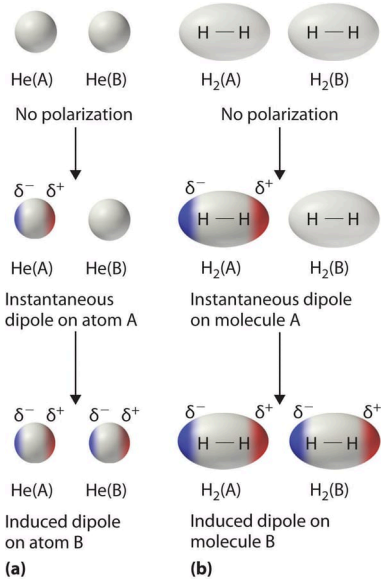


Figure 11.2.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 11.2.3, tends to become more pronounced as atomic and molecular masses increase (Table 11.2.2). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1s electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus, London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 11.2.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 11.2.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

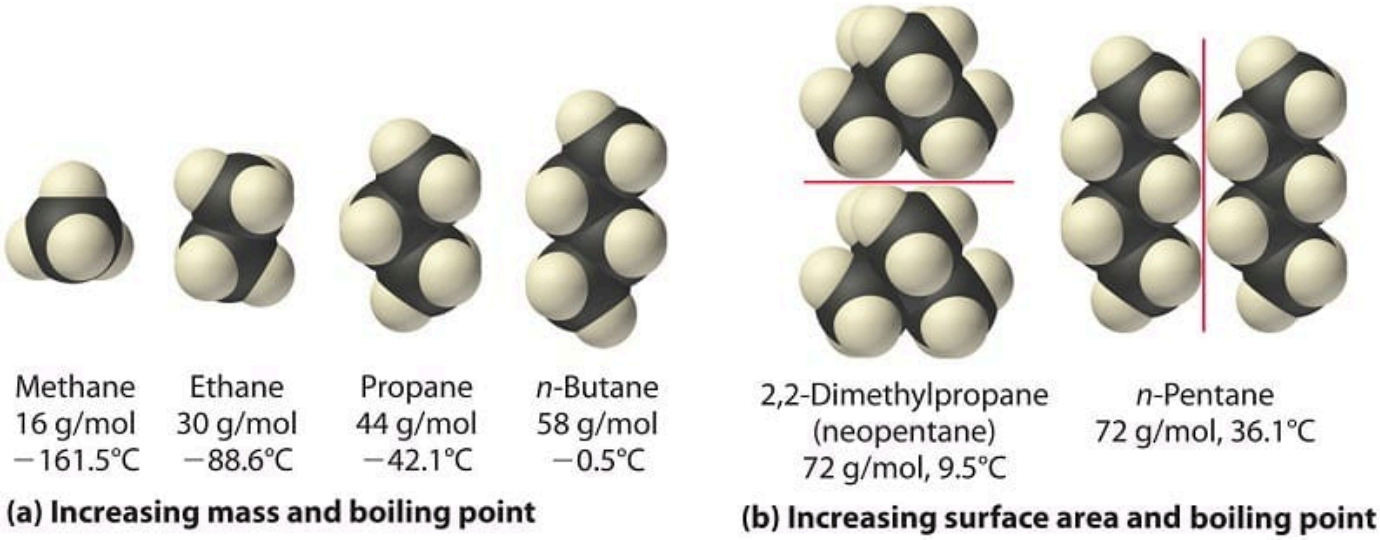


Figure 11.2.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

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Example 11.2.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds, and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

Exercise 11.2.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer available at the end of this section.

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent, Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 11.2.5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

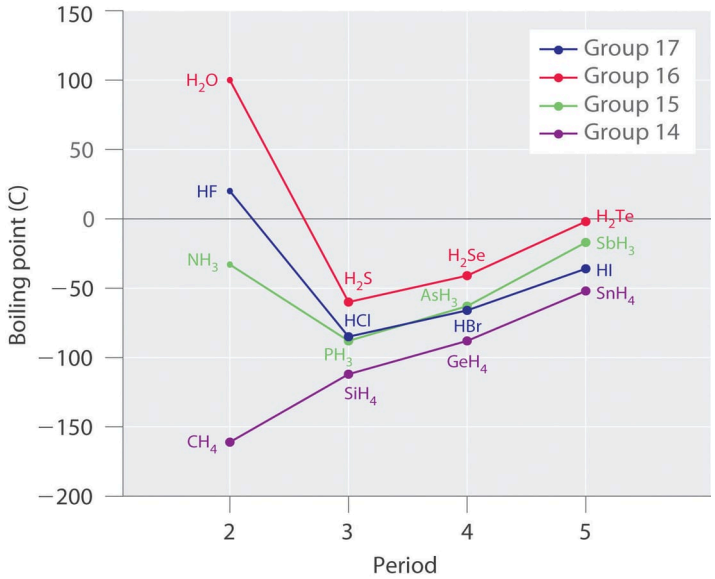


Figure 11.2.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Group 14 is in purple, group 15 is in green, group 16 is red, and group 17 is blue. Graph of boiling point against period.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these

dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 11.2.6. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O · · · H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water, rather than sinks.

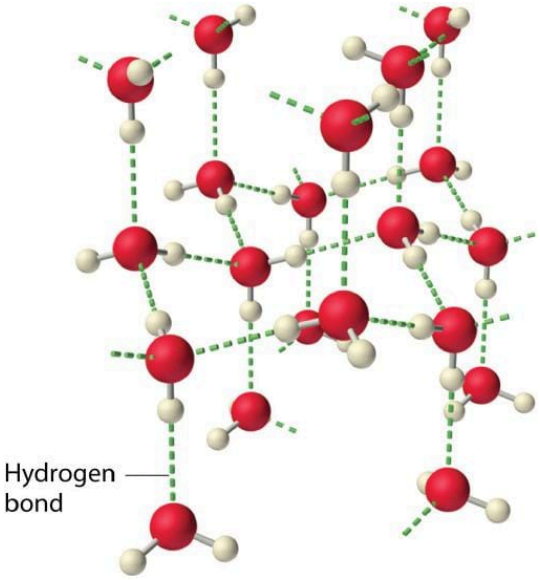


Figure 11.2.6: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cage like structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

YouTube Video

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Example 11.2.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

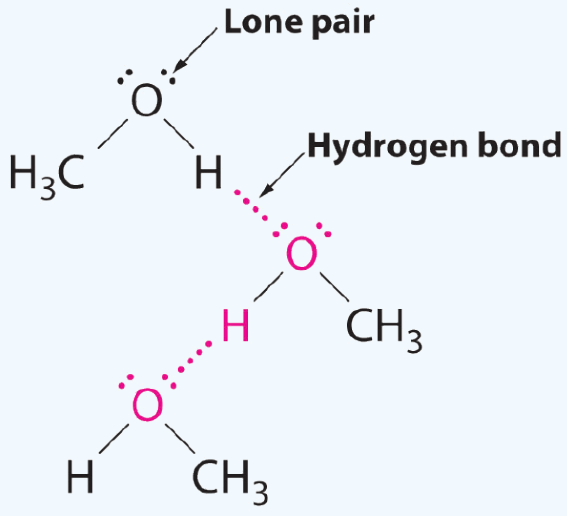
Strategy:

A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A. Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B. The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



Hydrogen bonding in methanol

Exercise 11.2.3

Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer available at the end of this section.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 11.2.4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$\text{He } (-269^\circ\text{C}) < \text{Ar } (-185.7^\circ\text{C}) < N_2O\ (-88.5^\circ\text{C}) < C_{60}\ (>280^\circ\text{C}) < \text{NaCl } (1465^\circ\text{C}).$$

Exercise 11.2.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer available at the end of this section.

Example 11.2.5

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.
b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.

c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

Exercise 11.2.6

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a available at the end of this section.

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid, or the liquid and gas phases, are due to changes in intermolecular interactions, but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^3$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules; their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones, because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O · · · H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cage like structure that is less dense than liquid water.

Answers

Exercise 11.2.1

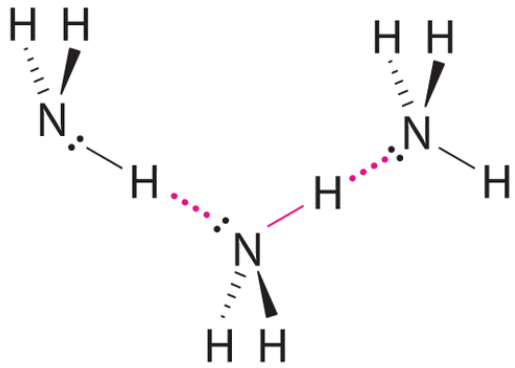
dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = –128°C)

Exercise 11.2.2

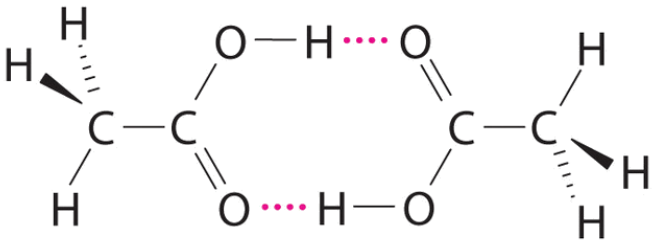
$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (–88.5°C) > SiH_4 (–111.8°C) > CH_4 (–161°C)

Exercise 11.2.3

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Hydrogen bonding in ammonia between nitrogen and hydrogen. hydrogen bonding in acetic acid is between oxygen and hydrogen.

Exercise 11.2.4

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (–34.6°C) > Ne (–246°C)

Exercise 11.2.6

hydrogen bonding

dipole-dipole interactions

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11.3: Some Properties of Liquids

Learning Objectives

- To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions:

- surface tension,
- capillary action, and
- viscosity.

Surface Tension

If liquids tend to adopt the shapes of their containers, then why do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of 7.29 x 10^{-2} J/m^2 (at 20°C), while mercury with metallic bonds has as surface tension that is 15 times higher: 4.86 x 10^{-1} J/m^2 (at 20°C).

Figure 11.3.1 presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

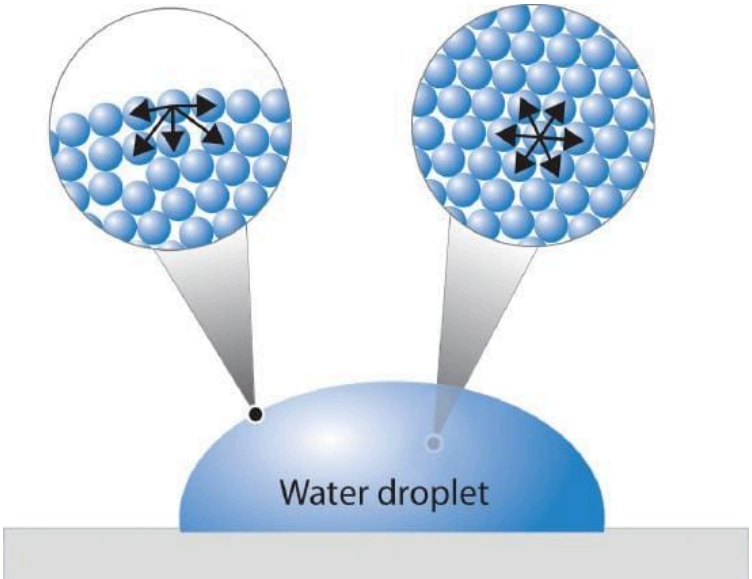


Figure 11.3.1: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it "floats," even though steel is much denser than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is even observable in the zero gravity conditions of space as shown in Figure 11.3.2 (and more so in the video link) where water wrung from a wet towel continues to float along the towel's surface!



Figure 11.3.2: The Effects of the High Surface Tension of Liquid Water. The full video can be found at www.youtube.com/watch?v=9jB7rOC5kG8.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2) or dyne per centimeter (dyn/cm), where 1 dyn = 1×10^{-5} N. The values of the surface tension of some representative liquids are listed in Table 11.3.1. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

Table 11.3.1: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension ($\times 10^{-3}$ J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				

Substance	Surface Tension (× 10^{-3} J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using "foams," which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure 11.3.3. When a glass capillary is is placed in liquid water, water rises up into the capillary. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

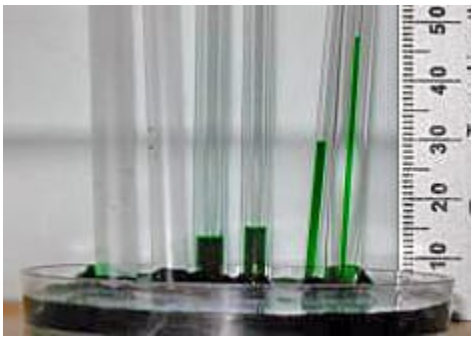


Figure 11.3.3: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.

- Cohesive forces bind molecules of the same type together
- Adhesive forces bind a substance to a surface

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (Figure 11.3.4). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure 11.3.4).

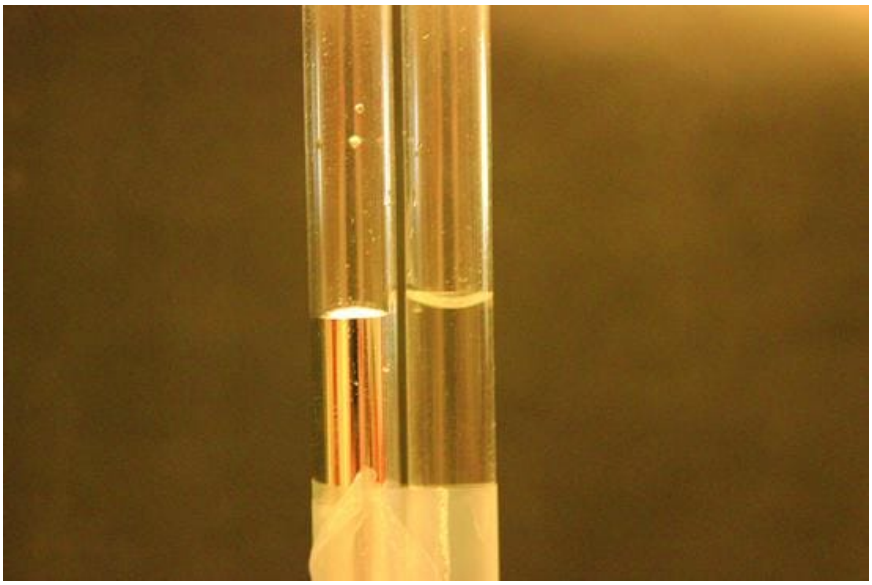


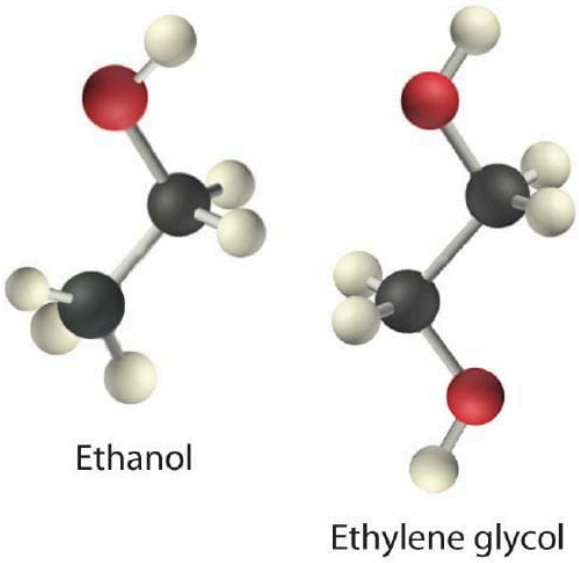
Figure 11.3.4: The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

> Polar substances are drawn up a glass capillary and generally have a concave meniscus.

Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and "wick" the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 11.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

Viscosity increases as intermolecular interactions or molecular size increases.

YouTube Video

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Video Discussing Surface Tension and Viscosity. Video Link: Surface Tension, Viscosity, & Melting Point, YouTube(opens in new window) [youtu.be]

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures.



Figure 11.3.5: Oil being drained from a car

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity (Figure 11.3.5). So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives "for improved engine performance" are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

Example 11.3.1

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A. Identify the cohesive forces in the motor oil.
B. Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains.

B Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

Exercise 11.3.1

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer available at the end of this section.

Summary

Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. **Surface tension** is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

Answers

Exercise 11.3.1

Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

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11.4: Phase Changes

Learning Objectives

- To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changes. The six most common phase changes are shown in Figure 11.4.1.

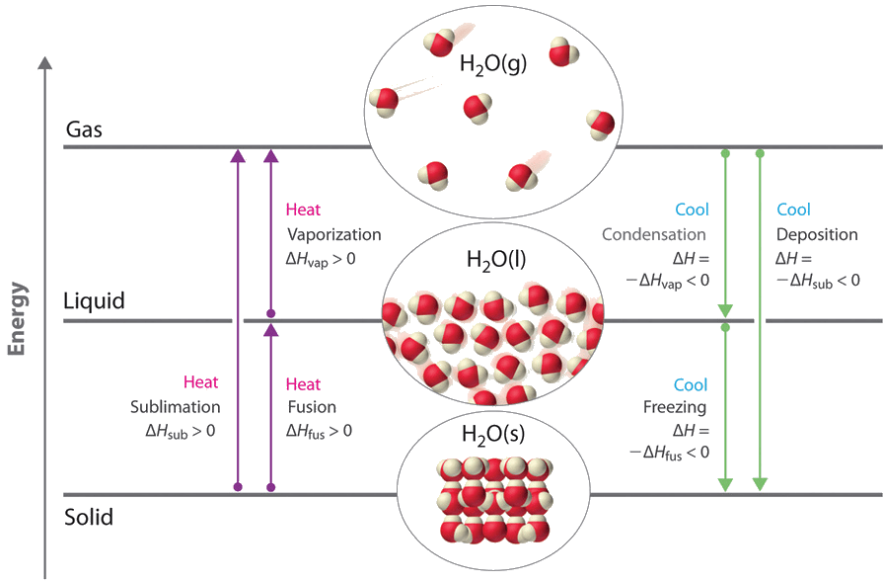


Figure 11.4.1: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. Purple arrows indicate heating from solid to gas, solid to liquid, and liquid to gas. Green arrows indicate cooling from gas to solid, gas to liquid, and liquid to solid. (CC BY-SA-NC; anoymous)

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure 11.4.1.

> ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The melting points and molar **enthalpies of fusion** (ΔH_{fus}), the energy required to convert from a solid to a liquid, a process known as fusion (or melting), as well as the normal boiling points and enthalpies of vaporization (ΔH_{vap}) of selected compounds are listed in Table 11.4.1.

Table 11.4.1: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

Less energy is needed to allow molecules to move past each other than to separate them totally.



Figure 11.4.2: The Sublimation of solid iodine. When solid iodine is heated at ordinary atmospheric pressure, it sublimes. When the I_2 vapor comes in contact with a cold surface, it deposits I_2 crystals. Figure used with permission from Wikipedia.

The direct conversion of a solid to a gas, without an intervening liquid phase, is called sublimation. The amount of energy required to sublime 1 mol of a pure solid is the enthalpy of sublimation (ΔH_{sub}). Common substances that sublime at standard temperature and pressure (STP; 0°C, 1 atm) include CO_2 (dry ice); iodine (Figure 11.4.2); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure 11.4.1, the enthalpy of sublimation of a substance is the sum of its enthalpies of fusion and vaporization provided all values are at the same *T*; this is an application of Hess's law.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{11.4.1}$$

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has

ever stepped out of a swimming pool on a cool, breezy day has felt the heat loss that accompanies the evaporation of water from the skin. Our bodies use this same phenomenon to maintain a constant temperature: we perspire continuously, even when at rest, losing about 600 mL of water daily by evaporation from the skin. We also lose about 400 mL of water as water vapor in the air we exhale, which also contributes to cooling. Refrigerators and air-conditioners operate on a similar principle: heat is absorbed from the object or area to be cooled and used to vaporize a low-boiling-point liquid, such as ammonia or the chlorofluorocarbons (CFCs) and the hydrofluorocarbons (HCFCs). The vapor is then transported to a different location and compressed, thus releasing and dissipating the heat. Likewise, ice cubes efficiently cool a drink not because of their low temperature but because heat is required to convert ice at 0°C to liquid water at 0°C.

Temperature Curves

The processes on the right side of Figure 11.4.1—freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure 11.4.3 shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and –23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

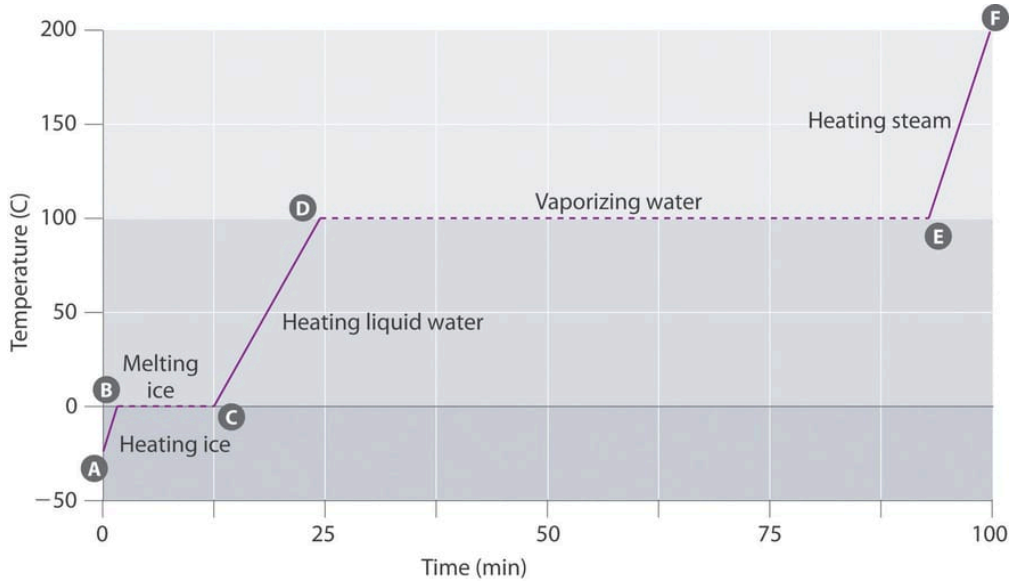


Figure 11.4.3: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and –23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if

the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

The temperature of a sample does not change during a phase change.

If heat is added at a constant rate, as in Figure 11.4.3, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 11.4.3, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure 11.4.4 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 11.4.3, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

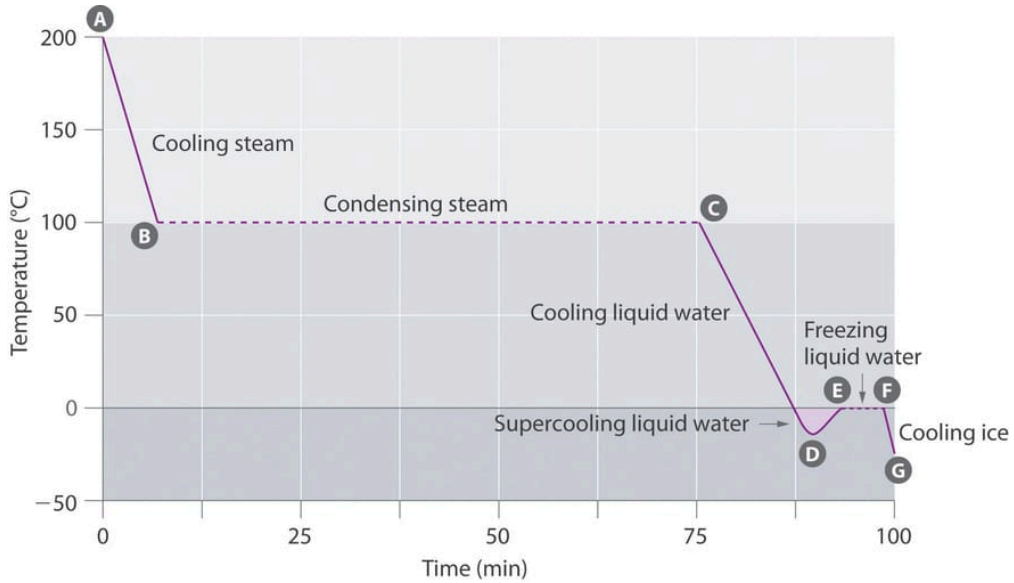


Figure 11.4.4: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth’s climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water,

which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about –10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.

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A Video Discussing the Thermodynamics of Phase Changes. Video Source: The Thermodynamics of Phase Changes, YouTube(opens in new window) [youtu.be]

Example 11.4.1: Cooling Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy

Substitute the given values into the general equation relating heat gained (by the ice) to heat lost (by the tea) to obtain the final temperature of the mixture.

Solution

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

The amount of heat gained by the ice cube as it melts is determined by its enthalpy of fusion in kJ/mol:

$$q = n\Delta H_{fus}$$

For our 50.0 g ice cube:

$$q_{ice} = 50.0g \cdot \frac{1\ mol}{18.02\ g} \cdot 6.01\ kJ/mol$$
$$= 16.7\,kJ$$

Thus, when the ice cube has just melted, it has absorbed 16.7 kJ of heat from the tea. We can then substitute this value into the first equation to determine the change in temperature of the tea:

$$q_{tea} = -16,700J = 500mL \cdot \frac{1.00\ g}{1\ mL} \cdot 4.184J/(g\bullet°C)\Delta T$$
$$\Delta T = -7.98°C = T_f - T_i$$
$$= 12.02°C$$

This would be the temperature of the tea when the ice cube has just finished melting; however, this leaves the melted ice still at 0.0°C. We might more practically want to know what the final temperature of the mixture of tea will be once the melted ice has come to thermal equilibrium with the tea. To determine this, we can add one more step to the calculation by plugging in to the general equation relating heat gained and heat lost again:

$$q_{ice} = -q_{tea}$$
$$q_{ice} = m_{ice}C_s\Delta T = 50.0g \cdot 4.184J/(g\bullet°C) \cdot (T_f - 0.0°C)$$
$$= 209.2J/°C \cdot T_f$$

$$q_{tea} = m_{tea}C_s\Delta T = 500g \cdot 4.184J/(g\bullet°C) \cdot (T_f - 12.02°C) = 2092J/°C \cdot T_f - 25,150J$$

$$209.2J/°C \cdot T_f = -2092J/°C \cdot T_f + 25,150J$$

$$2301.2J/°C \cdot T_f = 25,150J$$

$$T_f = 10.9°C$$

The final temperature is in between the initial temperatures of the tea (12.02 °C) and the melted ice (0.0 °C), so this answer makes sense. In this example, the tea loses much more heat in melting the ice than in mixing with the cold water, showing the importance of accounting for the heat of phase changes!

Exercise 11.4.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at –5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at –5.0°C to your body's internal temperature of 37°C. Use the data in Example 11.4.1

Answer available at the end of this section.

Summary

Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes. Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion (ΔH_{fus}). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization (ΔH_{vap}). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation (ΔH_{sub})** and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should

be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

Answers

Exercise 11.4.1**: Death by Freezing**

200 kJ (4.1 kJ to bring the ice from –5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

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11.5: Vapor Pressure

Learning Objectives

- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- To understand that the relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressure of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (*KE*) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure $11.5.1$), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

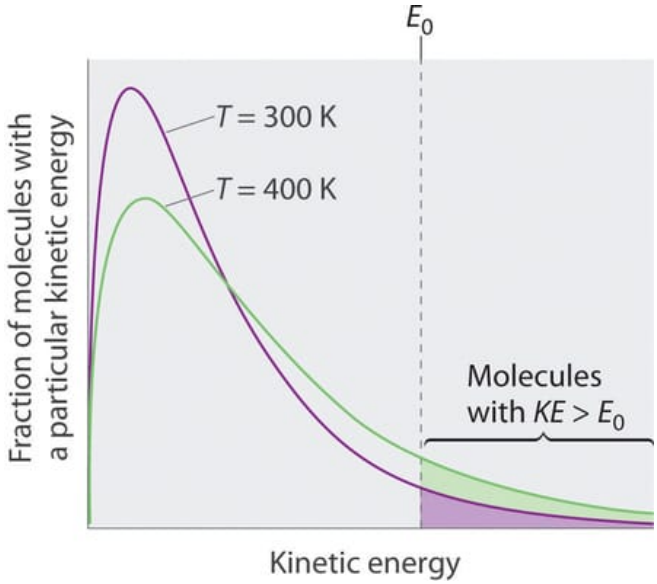


Figure 11.5.1: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature. (CC BY-SA-NC; Anonymous by request)

Graph of fraction of molecules with a particular kinetic energy against kinetic energy. Green line is temperature at 400 kelvin, purple line is temperature at 300 kelvin.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 11.5.2. When a liquid is introduced into an evacuated chamber (part (a) in Figure 11.5.2), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

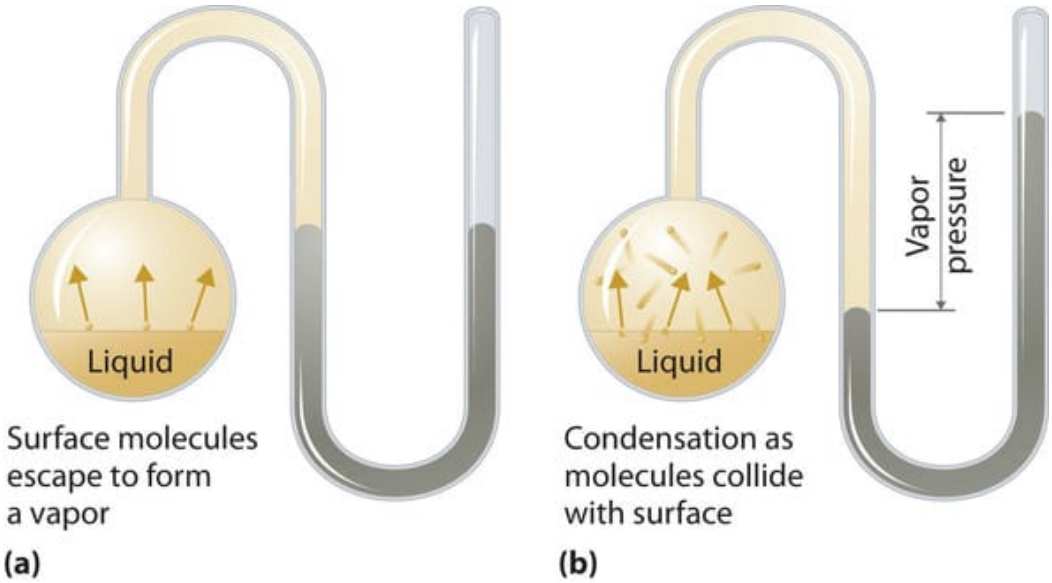


Figure 11.5.2: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant. (CC BY-SA-NC; Anonymous by request)

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure 11.5.2). As the number of molecules in the

vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure 11.5.3.

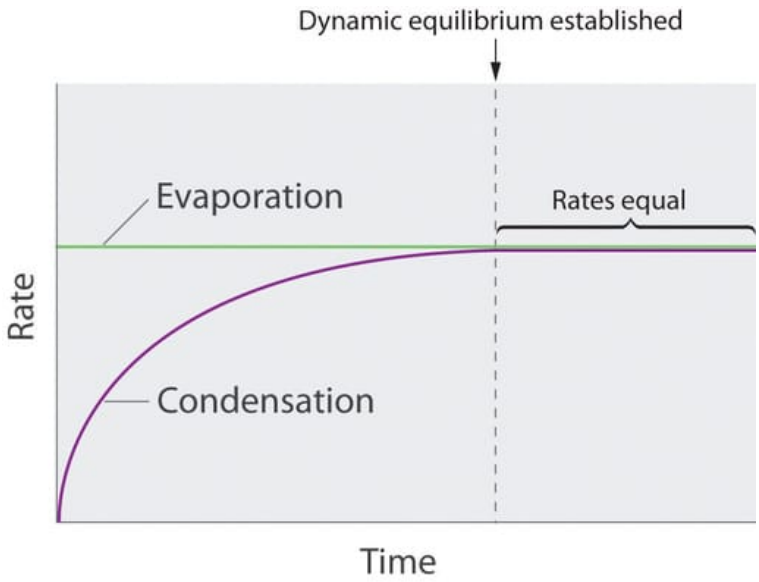


Figure 11.5.3: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation. (CC BY-SA-NC; Anonymous by request)

Graph of rate against time. The green line is evaporation while the pruple line is condensation. Dynamic equilibrium is established when the evaporation and condensation rates are equal.

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has “disappeared.” The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Figure 11.5.4) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

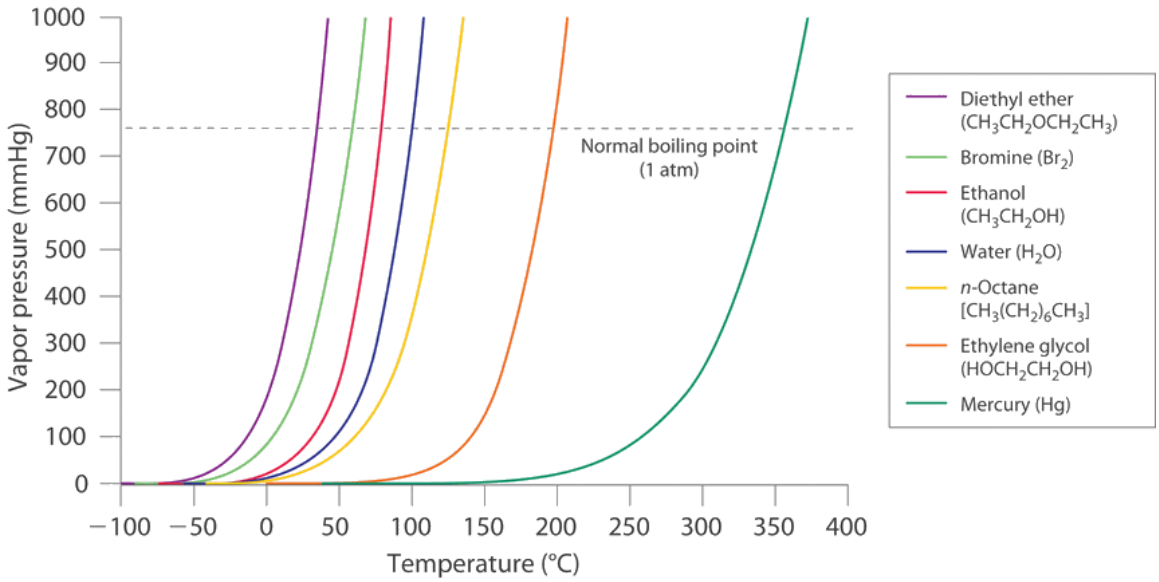


Figure 11.5.4: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the *P* = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; Anonymous by request)

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 11.5.4. Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

> Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.

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A Video Discussing Vapor Pressure and Boiling Points. Video Source: Vapor Pressure & Boiling Point(opens in new window) [youtu.be]

The exponential rise in vapor pressure with increasing temperature in Figure 11.5.4 allows us to use natural logarithms to express the nonlinear relationship as a linear one.

$$\boxed{\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C} \tag{11.5.1}$$

where

- $\ln P$ is the natural logarithm of the vapor pressure,
- ΔH_{vap} is the enthalpy of vaporization,
- R is the universal gas constant [8.314 J/(mol•K)],
- T is the temperature in kelvins, and
- C is the y-intercept, which is a constant for any given line.

Plotting $\ln P$ versus the inverse of the absolute temperature $(1/T)$ is a straight line with a slope of $-\Delta H_{vap}/R$. Equation 11.5.1, called the Clausius–Clapeyron Equation, can be used to calculate the ΔH_{vap} of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine ΔH_{vap} is to measure the vapor pressure of a liquid at **two** temperatures and insert the values of P and T for these points into Equation 11.5.2, which is derived from the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{11.5.2}$$

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation 11.5.2 to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example 11.5.1.

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A Video Discussing the Clausius-Clapeyron Equation. Video Link: The Clausius-Clapeyron Equation(opens in new window) [youtu.be]

Example 11.5.1: Vapor Pressure of Mercury

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

experimentally measured vapor pressures of liquid Hg at four temperatures

T (°C)	80.0	100	120	140
P (torr)	0.0888	0.2729	0.7457	1.845

From these data, calculate the enthalpy of vaporization (ΔH_{vap}) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

Given: vapor pressures at four temperatures

Asked for: ΔH_{vap} of mercury and vapor pressure at 160°C

Strategy:

A. Use Equation 11.5.2 to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.
B. Substitute the calculated value of ΔH_{vap} into Equation 11.5.2 to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 11.5.1 and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 11.5.2 to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvin because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 11.5.2 gives

$$\ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot K}\left(\frac{1}{(120+273)\ K} - \frac{1}{(80.0+273)\ K}\right)$$

$$\ln(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot \cancel{K}}\left(-2.88 \times 10^{-4}\ \cancel{K^{-1}}\right)$$

$$2.13 = -\Delta H_{vap}\left(-3.46 \times 10^{-4}\right) J^{-1} \cdot mol$$

$$\Delta H_{vap} = 61,400\ J/mol = 61.4\ kJ/mol$$

B We can now use this value of ΔH_{vap} to calculate the vapor pressure of the liquid (P_2) at 160.0°C (T_2):

$$\ln\left(\frac{P_2}{0.0888\ torr}\right) = \frac{-61,400\ \cancel{J/mol}}{8.314\ \cancel{J/mol}\ K^{-1}}\left(\frac{1}{(160+273)\ K} - \frac{1}{(80.0+273)\ K}\right)$$

Using the relationship $e^{\ln x} = x$, we have

$$\ln\left(\frac{P_2}{0.0888\ Torr}\right) = 3.86$$

$$\frac{P_2}{0.0888\ Torr} = e^{3.86} = 47.5$$

$$P_2 = 4.21 Torr$$

At 160°C, liquid Hg has a vapor pressure of 4.21 torr, substantially greater than the pressure at 80.0°C, as we would expect.

Exercise 11.5.1: Vapor Pressure of Nickel

The vapor pressure of liquid nickel at 1606°C is 0.100 torr, whereas at 1805°C, its vapor pressure is 1.000 torr. At what temperature does the liquid have a vapor pressure of 2.500 torr?

Answer available at the end of this section.

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure 11.5.4 are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table 11.5.1: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	–1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table 11.5.1 lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a "three-minute egg" may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

As pressure increases, the boiling point of a liquid increases and vice versa.

Example 11.5.2: Boiling Mercury

Use Figure 11.5.4 to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C



Mercury boils at 356 °C at room pressure. To see video go to www.youtube.com/watch?v=0iizsbXWYoo

Given: Data in Figure 11.5.4, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure 11.5.4 and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.

B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.
b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

Exercise 11.5.2: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure 11.5.4 to estimate the following.

a. the normal boiling point of ethylene glycol
b. the pressure required for diethyl ether to boil at 20°C.

Answer a available at the end of this section.

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 11.5.1: Vapor Pressure of Nickel

1896°C

Exercise 11.5.2: Boiling Ethlyene Glycol

200°C

450 mmHg

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11.6: Phase Diagrams

Learning Objectives

- To understand the basics of a one-component phase diagram as a function of temperature and pressure in a closed system.
- To be able to identify the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical fluid.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure 11.6.1). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure 11.6.1) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

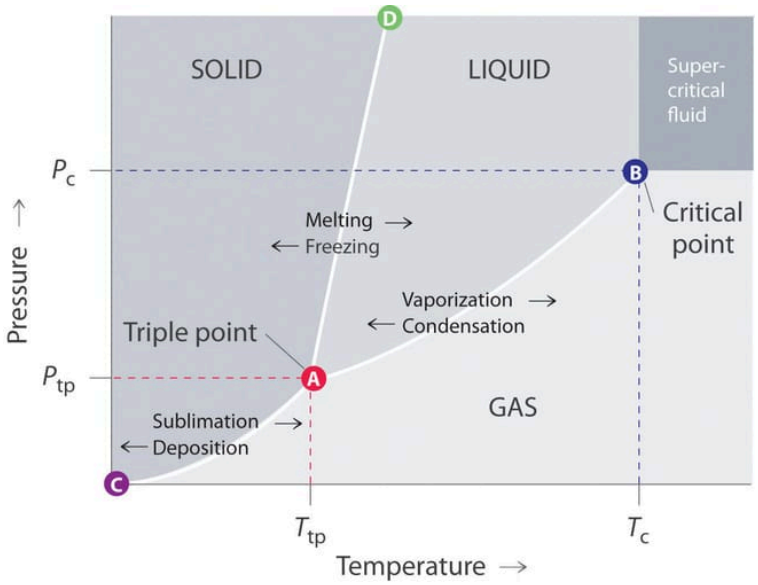


Figure 11.6.1: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure 11.6.1, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure 11.6.1, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure 11.6.2 shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

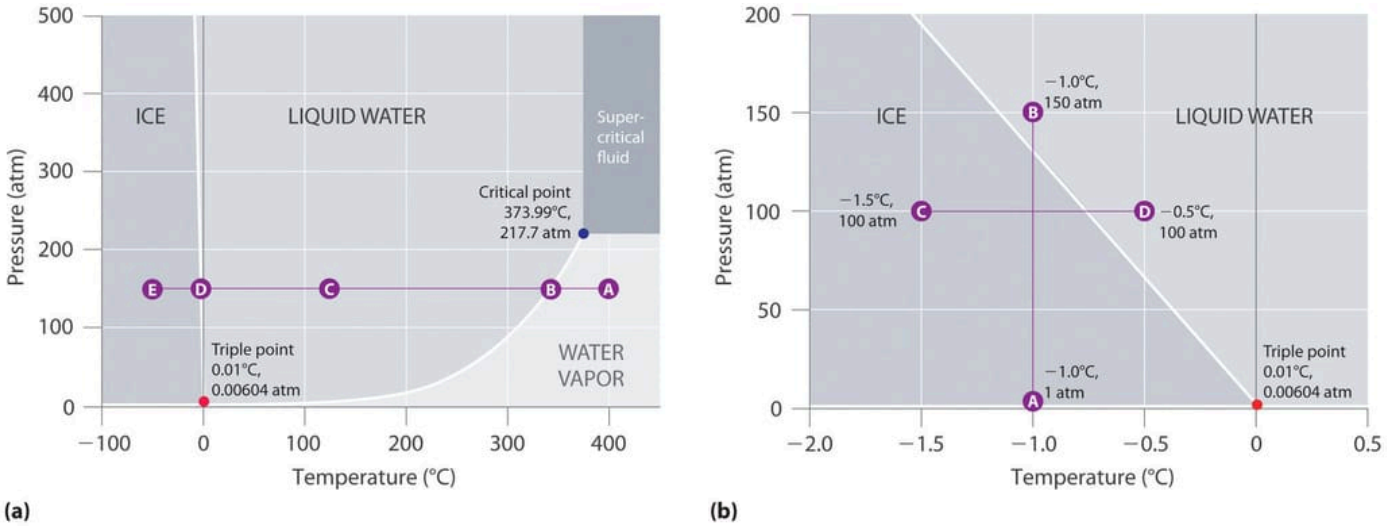


Figure 11.6.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 11.6.1).

The phase diagram for water illustrated in Figure 11.6.2*b* shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure 11.6.1; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure 11.6.2*b* point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would

sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Ice Skating: An Incorrect Hypothesis of Phase Transitions

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater's blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively satisfying, it is incorrect, as we can show by a simple calculation.



Pressure from ice skates on ice. from wikihow.com.

Recall that pressure (*P*) is the force (*F*) applied per unit area (*A*):

$$P = \frac{F}{A}$$

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

$$F = mg$$

where *m* is the mass and *g* is the acceleration due to Earth's gravity (9.81 m/s^2). Thus the force is

$$F = (75.0\ kg)(9.81\ m/s^2) = 736\ (kg \bullet m)/s^2 = 736N$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

$$A = (2.0 \times 10^{-3}\ m)(25 \times 10^{-2}\ m) = 5.0 \times 10^{-4} m^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

$$P = \frac{736\ N}{5.0 \times 10^{-4}\ m^2} = 1.5 \times 10^6\ N/m^2 = 1.5 \times 10^6\ Pa = 15\ atm$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C, and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water.

These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about −7°C, when the number of lubricating surface water layers decreases.

Example 11.6.1: Water

Referring to the phase diagram of water in Figure 11.6.2:

a. predict the physical form of a sample of water at 400°C and 150 atm.
b. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A. Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.
B. Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

a. **A** Locate the starting point on the phase diagram in part (a) in Figure 11.6.2. The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at T = 400°C and P = 150 atm is a gas.
b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure 11.6.2 . At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At P = 150 atm and T = −50°C, therefore, the sample is solid ice.

Exercise 11.6.2

Referring to the phase diagram of water in Figure 11.6.2, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer available at the end of this section.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure 11.6.3) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.



Dry ice ($CO_2\,(s)$) sublimed in air under room temperature and pressure. from Wikipedia.

Also notice the critical point at 30.98°C and 72.79 atm. Supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

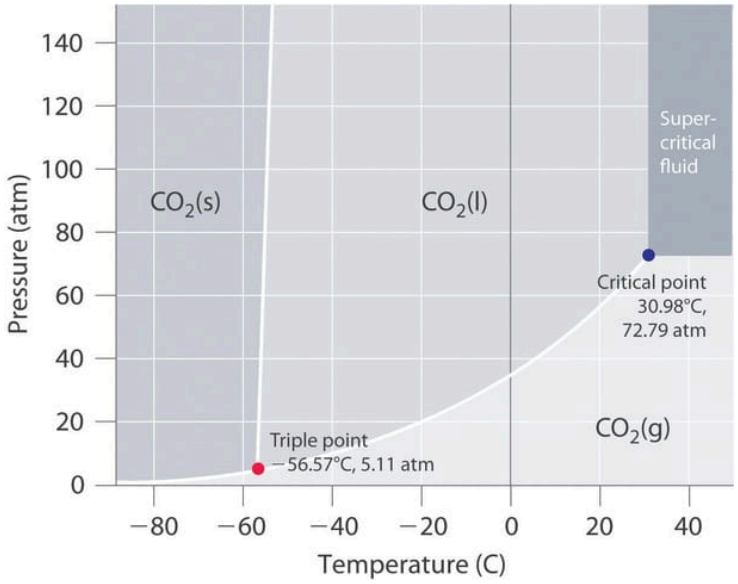


Figure 11.6.3: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

The triple point is at -57.57 degrees C and 5.11 atm. The critical point is at 30.98 degree C and 72.79 atm.

The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with

weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure 11.6.1.

Figure 11.6.1: Critical Temperatures and Pressures of Some Simple Substances

Substance	T_c (°C)	P_c (atm)
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.

Supercritical Fluids

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

A Video Discussing Phase Diagrams. Video Source: Phase Diagrams(opens in new window) [youtu.be]

Answers

Exercise 11.6.2

The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

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11.7: Structure of Solids

Learning Objectives

- To know the characteristic properties of crystalline and amorphous solids.
- To recognize the unit cell of a crystalline solid.
- To calculate the density of a solid given its unit cell.

Crystalline solids have regular ordered arrays of components held together by uniform intermolecular forces, whereas the components of amorphous solids are not arranged in regular arrays. With few exceptions, the particles that compose a solid material, whether ionic, molecular, covalent, or metallic, are held in place by strong attractive forces between them. When we discuss solids, therefore, we consider the positions of the atoms, molecules, or ions, which are essentially fixed in space, rather than their motions (which are more important in liquids and gases). The constituents of a solid can be arranged in two general ways: they can form a regular repeating three-dimensional structure called a crystal lattice, thus producing a crystalline solid, or they can aggregate with no particular order, in which case they form an amorphous solid (from the Greek ámorphos, meaning “shapeless”).



Figure 11.7.1: (left) Crystalline faces. The faces of crystals can intersect at right angles, as in galena (PbS) and pyrite (FeS_2), or at other angles, as in quartz. (Right) Cleavage surfaces of an amorphous solid. Obsidian, a volcanic glass with the same chemical composition as granite (typically $KAlSi_3O_8$), tends to have curved, irregular surfaces when cleaved.

Crystalline solids, or crystals, have distinctive internal structures that in turn lead to distinctive flat surfaces, or faces. The faces intersect at angles that are characteristic of the substance. When exposed to x-rays, each structure also produces a distinctive pattern that can be used to identify the material. The characteristic angles do not depend on the size of the crystal; they reflect the regular repeating arrangement of the component atoms, molecules, or ions in space. When an ionic crystal is cleaved (Figure 11.7.2, for example, repulsive interactions cause it to break along fixed planes to produce new faces that intersect at the same angles as those in the original crystal. In a covalent solid such as a cut diamond, the angles at which the faces meet are also not arbitrary but are determined by the arrangement of the carbon atoms in the crystal.

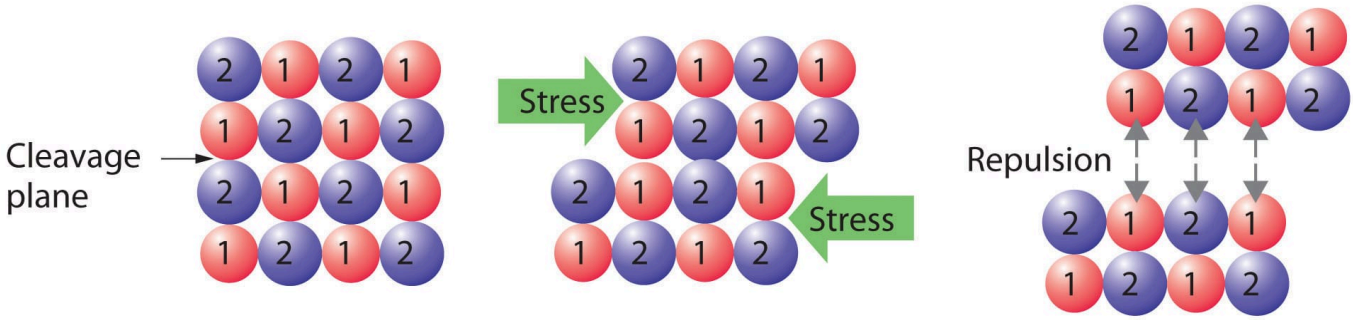


Figure 11.7.2: Cleaving a Crystal of an Ionic Compound along a Plane of Ions. Deformation of the ionic crystal causes one plane of atoms to slide along another. The resulting repulsive interactions between ions with like charges cause the layers to separate.

Crystals tend to have relatively sharp, well-defined melting points because all the component atoms, molecules, or ions are the same distance from the same number and type of neighbors; that is, the regularity of the crystalline lattice creates local environments that are the same. Thus the intermolecular forces holding the solid together are uniform, and the same amount of thermal energy is needed to break every interaction simultaneously.

Amorphous solids have two characteristic properties. When cleaved or broken, they produce fragments with irregular, often curved surfaces; and they have poorly defined patterns when exposed to x-rays because their components are not arranged in a regular array. An amorphous, translucent solid is called a glass. Almost any substance can solidify in amorphous form if the liquid phase is cooled rapidly enough. Some solids, however, are intrinsically amorphous, because either their components cannot fit together well enough to form a stable crystalline lattice or they contain impurities that disrupt the lattice. For example, although the chemical composition and the basic structural units of a quartz crystal and quartz glass are the same—both are SiO_2 and both consist of linked SiO_4 tetrahedra—the arrangements of the atoms in space are not. Crystalline quartz contains a highly ordered arrangement of silicon and oxygen atoms, but in quartz glass the atoms are arranged almost randomly. When molten SiO_2 is cooled rapidly (4 K/min), it forms quartz glass, whereas the large, perfect quartz crystals sold in mineral shops have had cooling times of thousands of years. In contrast, aluminum crystallizes much more rapidly. Amorphous aluminum forms only when the liquid is cooled at the extraordinary rate of 4×10^{13} K/s, which prevents the atoms from arranging themselves into a regular array.

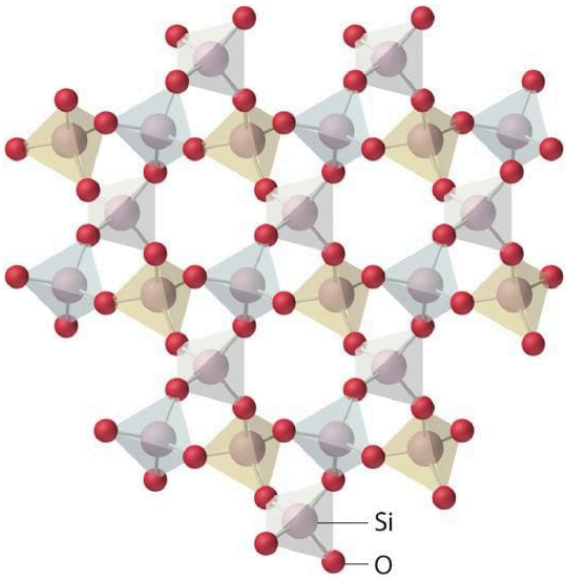


Figure 11.7.3: The lattice of crystalline quartz (SiO_2). The atoms form a regular arrangement in a structure that consists of linked tetrahedra.

In an amorphous solid, the local environment, including both the distances to neighboring units and the numbers of neighbors, varies throughout the material. Different amounts of thermal energy are needed to overcome these different interactions. Consequently, amorphous solids tend to soften slowly over a wide temperature range rather than having a well-defined melting point like a crystalline solid. If an amorphous solid is maintained at a temperature just below its melting point for long periods of time, the component molecules, atoms, or ions can gradually rearrange into a more highly ordered crystalline form.

Crystals have sharp, well-defined melting points; amorphous solids do not.

Crystals

Because a crystalline solid consists of repeating patterns of its components in three dimensions (a crystal lattice), we can represent the entire crystal by drawing the structure of the smallest identical units that, when stacked together, form the crystal. This basic repeating unit is called a unit cell. For example, the unit cell of a sheet of identical postage stamps is a single stamp, and the unit cell of a stack of bricks is a single brick. In this section, we describe the arrangements of atoms in various unit cells.

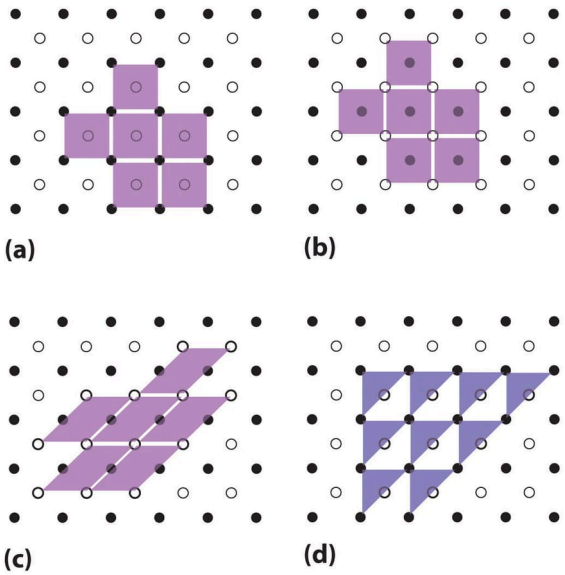


Figure 11.7.4: Unit Cells in Two Dimensions. (a–c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall pattern of dots. (d) The triangle is not a valid unit cell because repeating it in space fills only half of the space in the pattern.

Unit cells are easiest to visualize in two dimensions. In many cases, more than one unit cell can be used to represent a given structure, as shown for the Escher drawing in the chapter opener and for a two-dimensional crystal lattice in Figure 11.7.4. Usually the smallest unit cell that completely describes the order is chosen. The only requirement for a valid unit cell is that repeating it in space must produce the regular lattice. Thus the unit cell in Figure 11.7.4*d* is not a valid choice because repeating it in space does not produce the desired lattice (there are triangular holes). The concept of unit cells is extended to a three-dimensional lattice in the schematic drawing in Figure 11.7.5.

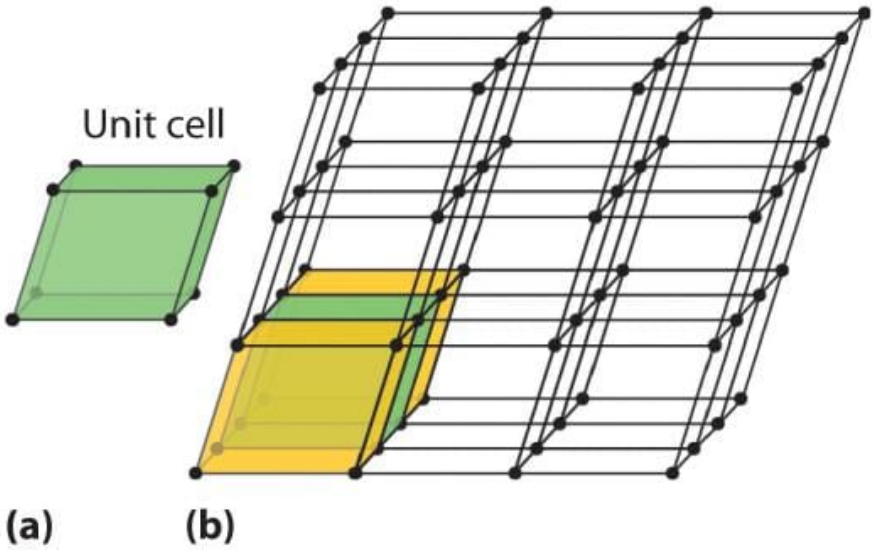


Figure 11.7.5: Unit Cells in Three Dimensions. These images show (a) a three-dimensional unit cell and (b) the resulting regular three-dimensional lattice.

The Unit Cell

There are seven fundamentally different kinds of unit cells, which differ in the relative lengths of the edges and the angles between them (Figure 11.7.6). Each unit cell has six sides, and each side is a parallelogram. We focus primarily on the cubic unit cells, in which all sides have the same length and all angles are 90°, but the concepts that we introduce also apply to substances whose unit cells are not cubic.

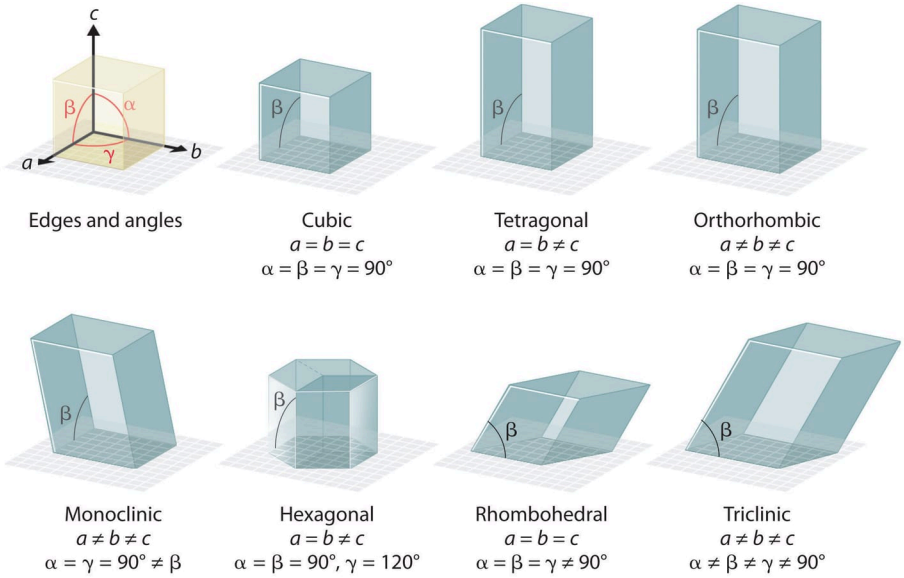


Figure 11.7.6: The General Features of the Seven Basic Unit Cells. The lengths of the edges of the unit cells are indicated by a, b, and c, and the angles are defined as follows: α, the angle between b and c; β, the angle between a and c; and γ, the angle between a and b.

Cubic: a = b=c, alpha= beta=gamma = 90 degrees. Tetragonal: a=b, alpha = beta = gamma = 90 degrees. Orthorhombic: alpha = beta = gamma = 90 degrees. Monoclinic: alpha = gamma = 90 degrees. Hexagonal: a = b, alpha = beta = 90 degrees, gamma = 120 degrees. Rhombohedral: a = b = c, alpha = beta= gamma. Triclinic: all different.

If the cubic unit cell consists of eight component atoms, molecules, or ions located at the corners of the cube, then it is called simple cubic (Figure 11.7.7*a*). If the unit cell also contains an identical component in the center of the cube, then it is body-centered cubic (bcc) (11.7.7*b*). If there are components in the center of each face in addition to those at the corners of the cube, then the unit cell is face-centered cubic (fcc) (Figure 11.7.7*c*).

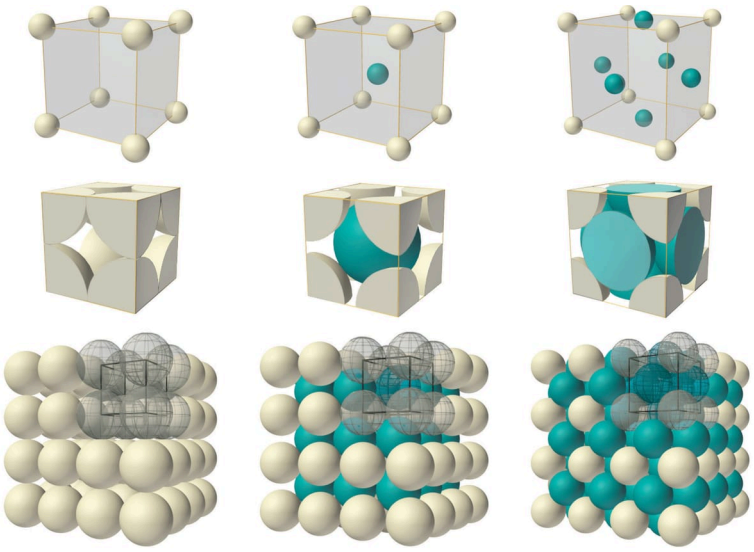


Figure 11.7.7: The Three Kinds of Cubic Unit Cell. For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that lies within the unit cell, and an aggregate of several unit cells.

Simple cubic is made of eight quarters of spheres. Body center cubic is made of eight quarters of spheers with a shpere in the middle. Face centered cubic is made of eight quarters of spheres and six half spheres.

As indicated in Figure 11.7.7, a solid consists of a large number of unit cells arrayed in three dimensions. Any intensive property of the bulk material, such as its density, must therefore also be related to its unit cell. Because density is the mass of substance per unit volume, we can calculate the density of the bulk material from the density of a single unit cell. To do this, we need to know the size of the unit cell (to obtain its volume), the molar mass of its components, and the number of components per unit cell. When we count atoms or ions in a unit cell, however, those lying on a face, an edge, or a corner contribute to more than one unit cell, as shown in Figure 11.7.7. For example, an atom that lies on a face of a unit cell is shared by two adjacent unit cells and is therefore counted as $\frac{1}{2}$ atom per unit cell. Similarly, an atom that lies on the edge of a unit cell is shared by four adjacent unit cells, so it contributes $\frac{1}{4}$ atom to each. An atom at a corner of a unit cell is shared by all eight adjacent unit cells and therefore contributes $\frac{1}{8}$ atom to each. The statement that atoms lying on an edge or a corner of a unit cell count as $\frac{1}{4}$ or $\frac{1}{8}$ atom per unit cell, respectively, is true for all unit cells except the hexagonal one, in which three unit cells share each vertical edge and six share each corner (Figure 11.7.7:), leading to values of $\frac{1}{3}$ and $\frac{1}{6}$ atom per unit cell, respectively, for atoms in these positions. In contrast, atoms that lie entirely within a unit cell, such as the atom in the center of a body-centered cubic unit cell, belong to only that one unit cell.

> For all unit cells except hexagonal, atoms on the faces contribute $\frac{1}{2}$ atom to each unit cell, atoms on the edges contribute $\frac{1}{4}$ atom to each unit cell, and atoms on the corners contribute $\frac{1}{8}$ atom to each unit cell.

Example 11.7.1: The Unit Cell for Gold

Metallic gold has a face-centered cubic unit cell (11.7.7c). How many Au atoms are in each unit cell?

Given: unit cell

Asked for: number of atoms per unit cell

Strategy

Using Figure 11.7.7, identify the positions of the Au atoms in a face-centered cubic unit cell and then determine how much each Au atom contributes to the unit cell. Add the contributions of all the Au atoms to obtain the total number of Au atoms in a unit cell.

Solution

As shown in Figure 11.7.7, a face-centered cubic unit cell has eight atoms at the corners of the cube and six atoms on the faces. Because atoms on a face are shared by two unit cells, each counts as $\frac{1}{2}$ atom per unit cell, giving $6 \times \frac{1}{2} = 3$ Au atoms per unit cell. Atoms on a corner are shared by eight unit cells and hence contribute only $\frac{1}{8}$ atom per unit cell, giving $8 \times \frac{1}{8} = 1$ Au atom per unit cell. The total number of Au atoms in each unit cell is thus $3 + 1 = 4$.

Exercise 11.7.1: Unit Cell for Iron

Metallic iron has a body-centered cubic unit cell (Figure 11.7.7*b*). How many Fe atoms are in each unit cell?

Answer available at the end of this section.

Now that we know how to count atoms in unit cells, we can use unit cells to calculate the densities of simple compounds. Note, however, that we are assuming a solid consists of a perfect regular array of unit cells, whereas real substances contain impurities and defects that affect many of their bulk properties, including density. Consequently, the results of our calculations will be close but not necessarily identical to the experimentally obtained values.

Example 11.7.2: Density of Iron

Calculate the density of metallic iron, which has a body-centered cubic unit cell (Figure 11.7.7*b*) with an edge length of 286.6 pm.

Given: unit cell and edge length

Asked for: density

Strategy:

A. Determine the number of iron atoms per unit cell.
B. Calculate the mass of iron atoms in the unit cell from the molar mass and Avogadro's number. Then divide the mass by the volume of the cell.

Solution:

A We know from Example 11.7.1 that each unit cell of metallic iron contains two Fe atoms.

B The molar mass of iron is 55.85 g/mol. Because density is mass per unit volume, we need to calculate the mass of the iron atoms in the unit cell from the molar mass and Avogadro's number and then divide the mass by the volume of the cell (making sure to use suitable units to get density in g/cm^3):

$$mass\ of\ Fe = (2\ \cancel{atoms}\ Fe)\left(\frac{1\ \cancel{mol}}{6.022 \times 10^{23}\ \cancel{atoms}}\right)\left(\frac{55.85\ g}{\cancel{mol}}\right) = 1.855 \times 10^{-22}\ g$$

$$volume = \left[(286.6\ pm)\left(\frac{10^{-12}\ \cancel{m}}{\cancel{pm}}\right)\left(\frac{10^{2}\ cm}{\cancel{m}}\right)\right] = 2.345 \times 10^{-23}\ cm^3$$

$$density = \frac{1.855 \times 10^{-22}\ g}{2.345 \times 10^{-23}\ cm^3} = 7.880 g/cm^3$$

This result compares well with the tabulated experimental value of 7.874 g/cm^3.

Exercise 11.7.2: Density of Gold

Calculate the density of gold, which has a face-centered cubic unit cell (Figure 11.7.7*c*) with an edge length of 407.8 pm.

Answer available at the end of this section.

Packing of Spheres

Our discussion of the three-dimensional structures of solids has considered only substances in which all the components are identical. As we shall see, such substances can be viewed as consisting of identical spheres packed together in space; the way the components are packed together produces the different unit cells. Most of the substances with structures of this type are metals.

Simple Cubic Structure

The arrangement of the atoms in a solid that has a simple cubic unit cell was shown in Figure $11.7.5a$. Each atom in the lattice has only six nearest neighbors in an octahedral arrangement. Consequently, the simple cubic lattice is an inefficient way to pack atoms together in space: only 52% of the total space is filled by the atoms. The only element that crystallizes in a simple cubic unit cell is polonium. Simple cubic unit cells are, however, common among binary ionic compounds, where each cation is surrounded by six anions and vice versa (Figure $11.7.8$).

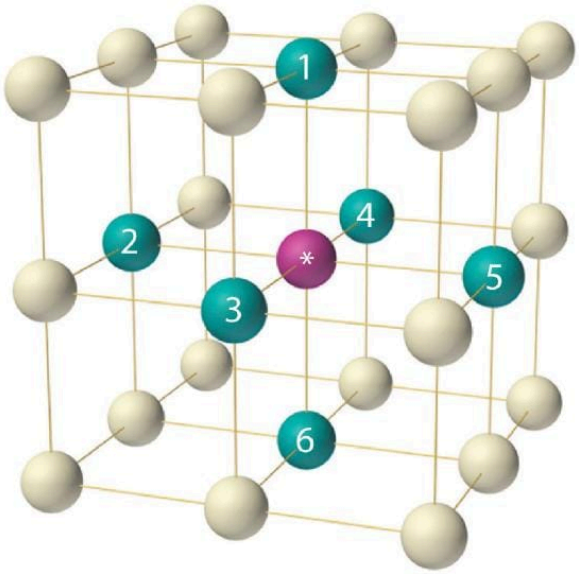


Figure $11.7.8$: The arrangement of atoms in a simple cubic unit cell. Each atom in the lattice has six nearest neighbors in an octahedral arrangement.

Body-Centered Cubic Structure

The body-centered cubic unit cell is a more efficient way to pack spheres together and is much more common among pure elements. Each atom has eight nearest neighbors in the unit cell, and 68% of the volume is occupied by the atoms. As shown in Figure $11.7.8$, the body-centered cubic structure consists of a single layer of spheres in contact with each other and aligned so that their centers are at the corners of a square; a second layer of spheres occupies the square-shaped “holes” above the spheres in the first layer. The third layer of spheres occupies the square holes formed by the second layer, so that each lies directly above a sphere in the first layer, and so forth. All the alkali metals, barium, radium, and several of the transition metals have body-centered cubic structures.

Hexagonal Close-Packed and Cubic Close-Packed Structures

The most efficient way to pack spheres is the close-packed arrangement, which has two variants. A single layer of close-packed spheres is shown in Figure $11.7.6a$. Each sphere is surrounded by six others in the same plane to produce a hexagonal arrangement. Above any set of seven spheres are six depressions arranged in a hexagon. In principle, all six sites are the same, and any one of them could be occupied by an atom in the next layer. Actually, however, these six sites can be divided into two

sets, labeled B and C in Figure 11.7.9*a*. Sites B and C differ because as soon as we place a sphere at a B position, we can no longer place a sphere in any of the three C positions adjacent to A and vice versa.

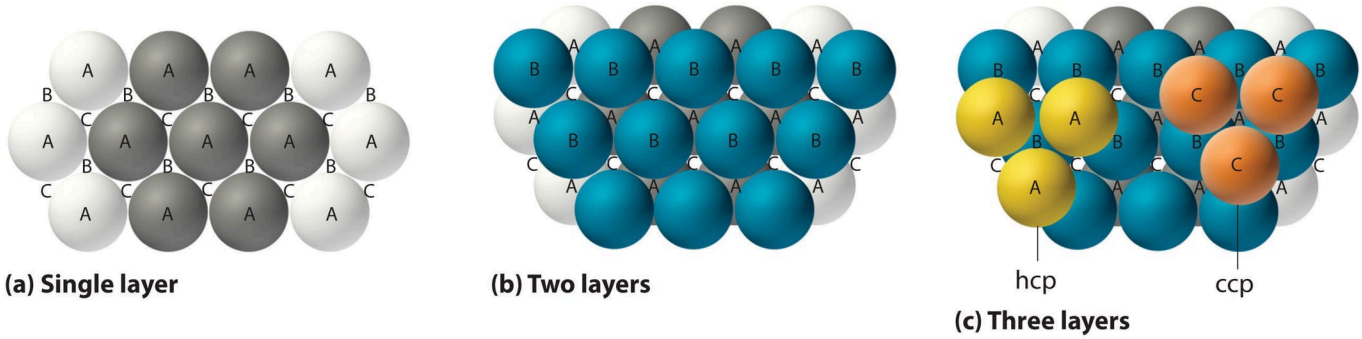


Figure 11.7.9: Close-Packed Layers of Spheres. (a) In this single layer of close-packed spheres, each sphere is surrounded by six others in a hexagonal arrangement. (b) Placing an atom at a B position prohibits placing an atom at any of the adjacent C positions and results in all the atoms in the second layer occupying the B positions. (c) Placing the atoms in the third layer over the atoms at A positions in the first layer gives the hexagonal close-packed structure. Placing the third-layer atoms over the C positions gives the cubic close-packed structure.

If we place the second layer of spheres at the B positions in Figure 11.7.9*a*, we obtain the two-layered structure shown in Figure 11.7.9*b*. There are now two alternatives for placing the first atom of the third layer: we can place it directly over one of the atoms in the first layer (an A position) or at one of the C positions, corresponding to the positions that we did not use for the atoms in the first or second layers (Figure 11.7.9*c*). If we choose the first arrangement and repeat the pattern in succeeding layers, the positions of the atoms alternate from layer to layer in the pattern ABABAB..., resulting in a hexagonal close-packed (hcp) structure (Figure 11.7.9*a*). If we choose the second arrangement and repeat the pattern indefinitely, the positions of the atoms alternate as ABCABC..., giving a cubic close-packed (ccp) structure (Figure 11.7.9*b*). Because the ccp structure contains hexagonally packed layers, it does not look particularly cubic. As shown in Figure 11.7.9*b*, however, simply rotating the structure reveals its cubic nature, which is identical to a fcc structure. The hcp and ccp structures differ only in the way their layers are stacked. Both structures have an overall packing efficiency of 74%, and in both each atom has 12 nearest neighbors (6 in the same plane plus 3 in each of the planes immediately above and below).

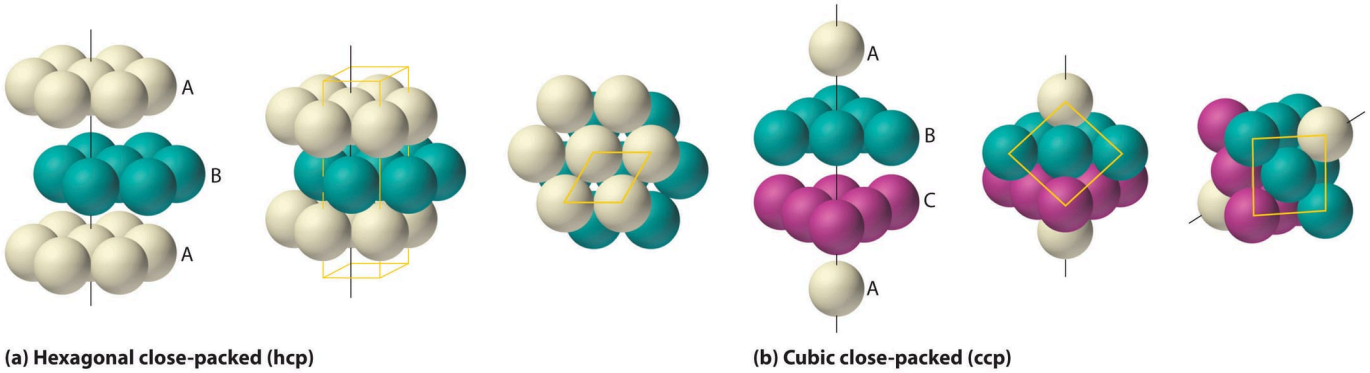


Figure 11.7.10. The ccp structure in (b) is shown in an exploded view, a side view, and a rotated view. The rotated view emphasizes the fcc nature of the unit cell (outlined). The line that connects the atoms in the first and fourth layers of the ccp structure is the body diagonal of the cube.

Table 11.7.1 compares the packing efficiency and the number of nearest neighbors for the different cubic and close-packed structures; the number of nearest neighbors is called the coordination number. Most metals have hcp, ccp, or bcc structures, although several metals exhibit both hcp and ccp structures, depending on temperature and pressure.

Table 11.7.1: Properties of the Common Structures of Metals

Structure	Percentage of Space Occupied by Atoms	Coordination Number
simple cubic	52	6
body-centered cubic	68	8

Structure	Percentage of Space Occupied by Atoms	Coordination Number
hexagonal close packed	74	12
cubic close packed (identical to face-centered cubic)	74	12

Summary

A crystalline solid can be represented by its unit cell, which is the smallest identical unit that when stacked together produces the characteristic three-dimensional structure. Solids are characterized by an extended three-dimensional arrangement of atoms, ions, or molecules in which the components are generally locked into their positions. The components can be arranged in a regular repeating three-dimensional array (a crystal lattice), which results in a crystalline solid, or more or less randomly to produce an amorphous solid. Crystalline solids have well-defined edges and faces, diffract x-rays, and tend to have sharp melting points. In contrast, amorphous solids have irregular or curved surfaces, do not give well-resolved x-ray diffraction patterns, and melt over a wide range of temperatures.

The smallest repeating unit of a crystal lattice is the unit cell. The simple cubic unit cell contains only eight atoms, molecules, or ions at the corners of a cube. A body-centered cubic (bcc) unit cell contains one additional component in the center of the cube. A face-centered cubic (fcc) unit cell contains a component in the center of each face in addition to those at the corners of the cube. Simple cubic and bcc arrangements fill only 52% and 68% of the available space with atoms, respectively. The hexagonal close-packed (hcp) structure has an ABABAB... repeating arrangement, and the cubic close-packed (ccp) structure has an ABCABC... repeating pattern; the latter is identical to an fcc lattice. The hcp and ccp arrangements fill 74% of the available space and have a coordination number of 12 for each atom in the lattice, the number of nearest neighbors. The simple cubic and bcc lattices have coordination numbers of 6 and 8, respectively.

Contributors and Attributions

- Template:Lard2

Answers

Exercise 11.7.1**: Unit Cell for Iron**

two

Exercise 11.7.2**: Density of Gold**

19.29 g/cm^3

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11.8: Bonding in Solids

Learning Objectives

- To understand the correlation between bonding and the properties of solids.
- To classify solids as ionic, molecular, covalent (network), or metallic, where the general order of increasing strength of interactions.

Crystalline solids fall into one of four categories. All four categories involve packing discrete molecules or atoms into a lattice or repeating array, though *network solids* are a special case. The categories are distinguished by the nature of the interactions holding the discrete molecules or atoms together. Based on the nature of the forces that hold the component atoms, molecules, or ions together, solids may be formally classified as ionic, molecular, covalent (network), or metallic. The variation in the relative strengths of these four types of interactions correlates nicely with their wide variation in properties.

Table 11.8.1*: Solids may be formally classified as ionic, molecular, covalent (network), or metallic*

Type of Solid	Interaction	Properties	Examples
Ionic	Ionic	High Melting Point, Brittle, Hard	NaCl, MgO
Molecular	Hydrogen Bonding, Dipole-Dipole, London Dispersion	Low Melting Point, Nonconducting	H_2, CO_2
Metallic	Metallic Bonding	Variable Hardness and Melting Point (depending upon strength of metallic bonding), Conducting	Fe, Mg
Network	Covalent Bonding	High Melting Point, Hard, Nonconducting	C (diamond), SiO_2 (quartz)

In ionic and molecular solids, there are no chemical bonds between the molecules, atoms, or ions. The solid consists of discrete chemical species held together by intermolecular forces that are **electrostatic** or **Coulombic** in nature. This behavior is most obvious for an ionic solid such as $NaCl$, where the positively charged Na^+ ions are attracted to the negatively charged Cl^- ions. Even in the absence of ions, however, electrostatic forces are operational. For polar molecules such as CH_2Cl_2, the positively charged region of one molecular is attracted to the negatively charged region of another molecule (dipole-dipole interactions). For a nonpolar molecule such as CO_2, which has no permanent dipole moment, the random motion of electrons gives rise to temporary polarity (a temporary dipole moment). Electrostatic attractions between two temporarily polarized molecules are called London Dispersion Forces.

Hydrogen bonding is a term describing an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. (See the IUPAC Provisional Recommendation on the definition of a hydrogen bond.) Dots are employed to indicate the presence of a hydrogen bond: X–H•••Y. The attractive interaction in a hydrogen bond typically has a strong electrostatic contribution, but dispersion forces and weak covalent bonding are also present.

In metallic solids and network solids, however, chemical bonds hold the individual chemical subunits together. The crystal is essential a single, macroscopic molecule with continuous chemical bonding throughout the entire structure. In metallic solids, the valence electrons are no longer exclusively associated with a single atom. Instead these electrons exist in molecular orbitals that are delocalized over many atoms, producing an electronic band structure. The metallic crystal essentially consists of a set of metal cations in a sea of electrons. This type of chemical bonding is called metallic bonding.

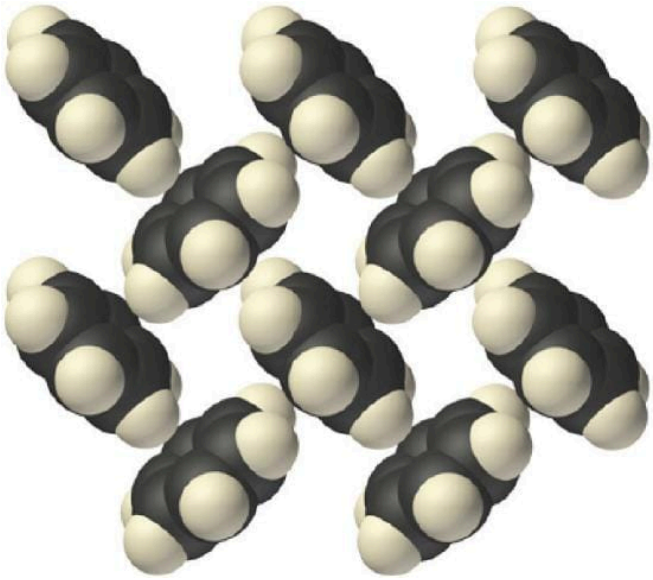
Ionic Solids

You learned previously that an ionic solid consists of positively and negatively charged ions held together by electrostatic forces. The strength of the attractive forces depends on the charge and size of the ions that compose the lattice and determines many of the physical properties of the crystal.

The **lattice energy** (i.e., the energy required to separate 1 mol of a crystalline ionic solid into its component ions in the gas phase) is directly proportional to the product of the ionic charges and inversely proportional to the sum of the radii of the ions. For example, NaF and CaO both crystallize in the face-centered cubic (fcc) sodium chloride structure, and the sizes of their component ions are about the same: Na^+ (102 pm) versus Ca^{2+} (100 pm), and F^- (133 pm) versus O^{2-} (140 pm). Because of the higher charge on the ions in CaO, however, the lattice energy of CaO is almost four times greater than that of NaF (3401 kJ/mol versus 923 kJ/mol). The forces that hold Ca and O together in CaO are much stronger than those that hold Na and F together in NaF, so the heat of fusion of CaO is almost twice that of NaF (59 kJ/mol versus 33.4 kJ/mol), and the melting point of CaO is 2927°C versus 996°C for NaF. In both cases, however, the values are large; that is, simple ionic compounds have high melting points and are relatively hard (and brittle) solids.

Molecular Solids

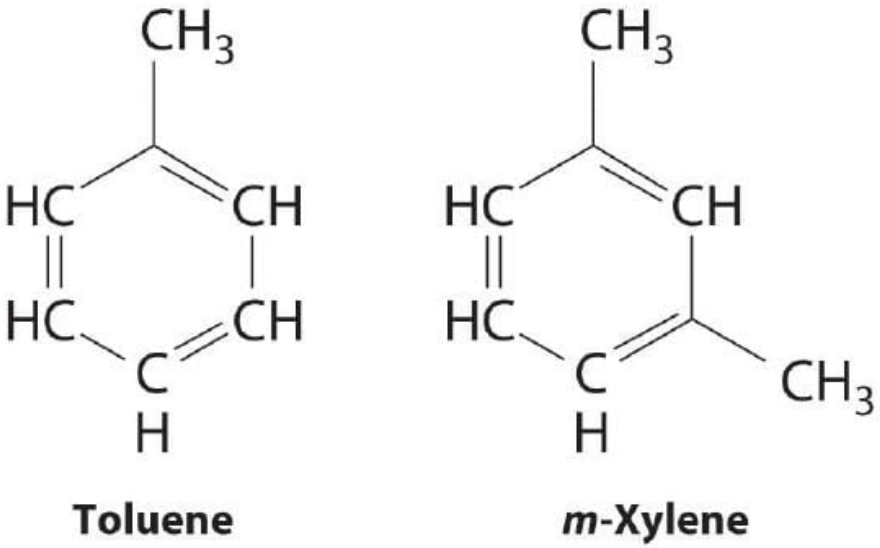
Molecular solids consist of atoms or molecules held to each other by dipole–dipole interactions, London dispersion forces, or hydrogen bonds, or any combination of these. The arrangement of the molecules in solid benzene is as follows:



The structure of solid benzene. In solid benzene, the molecules are not arranged with their planes parallel to one another but at 90° angles. (CC BY-NC-SA; Anonymous by request).

Because the intermolecular interactions in a molecular solid are relatively weak compared with ionic and covalent bonds, molecular solids tend to be soft, low melting, and easily vaporized (ΔH_{fus} and ΔH_{vap} are low). For similar substances, the strength of the London dispersion forces increases smoothly with increasing molecular mass. For example, the melting points of benzene (C_6H_6), naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$), with one, two, and three fused aromatic rings, are 5.5°C, 80.2°C, and 215°C, respectively. The enthalpies of fusion also increase smoothly within the series: benzene (9.95 kJ/mol) < naphthalene (19.1 kJ/mol) < anthracene (28.8 kJ/mol). If the molecules have shapes that cannot pack together efficiently in the crystal, however, then the melting points and the enthalpies of fusion tend to be unexpectedly low because the molecules are unable to arrange themselves to optimize intermolecular interactions. Thus toluene ($C_6H_5CH_3$) and m-xylene [m-$C_6H_4(CH_3)_2$] have melting points of −95°C and −48°C, respectively, which are significantly lower than the melting point of the lighter but more symmetrical analog, benzene.

Self-healing rubber is an example of a molecular solid with the potential for significant commercial applications. The material can stretch, but when snapped into pieces it can bond back together again through reestablishment of its hydrogen-bonding network without showing any sign of weakness. Among other applications, it is being studied for its use in adhesives and bicycle tires that will self-heal.



Toluene and m-xylene. The methyl groups attached to the phenyl ring in toluene and m-xylene prevent the rings from packing together as in solid benzene. (CC BY-NC-SA; Anonymous by request).

Covalent Network Solids

Covalent solids are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure 11.8.1, consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.

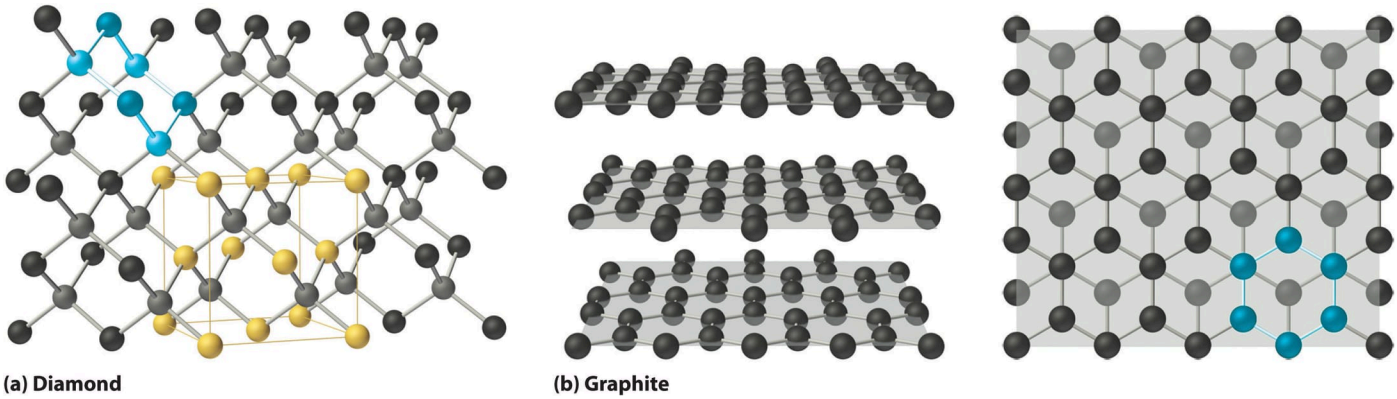


Figure 11.8.1: The Structures of Diamond and Graphite. (a) Diamond consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. This is easier to see in the rotating cube shown in Figure 11.8.2 below. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer. (CC BY-NC-SA; Anonymous by request).

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in Section 12.3, except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (SiO_2), shown in Section 12.1, can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is

used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in Figure 11.8.1. It contains planar networks of six-membered rings of sp2 hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized 2pz orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in Chapter 9. In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimes at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the “lead” in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other hand, is colorless when pure because it has no delocalized electrons. Table 11.8.2 compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table 11.8.2: A Comparison of Intermolecular (ΔH_{sub}) and Intramolecular Interactions

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
phosphorus (s)	58.98	201
sulfur (s)	64.22	226
iodine (s)	62.42	149

Carbon: An example of an Covalent Network Solid

In network solids, conventional chemical bonds hold the chemical subunits together. The bonding between chemical subunits, however, is identical to that within the subunits, resulting in a continuous network of chemical bonds. One common examples of network solids are diamond (a form of pure carbon) Carbon exists as a pure element at room temperature in three different forms: graphite (the most stable form), diamond, and fullerene.

Diamonds

The structure of diamond is shown at the right in a "ball-and-stick" format. The balls represent the carbon atoms and the sticks represent a covalent bond. Be aware that in the "ball-and-stick" representation the size of the balls do not accurately represent the size of carbon atoms. In addition, a single stick is drawn to represent a covalent bond irrespective of whether the bond is a single, double, or triple bond or requires resonance structures to represent. In the diamond structure, all bonds are single covalent bonds (σ bonds). The "space-filling" format is an alternate representation that displays atoms as spheres with a radius equal to the van der Waals radius, thus providing a better sense of the size of the atoms.

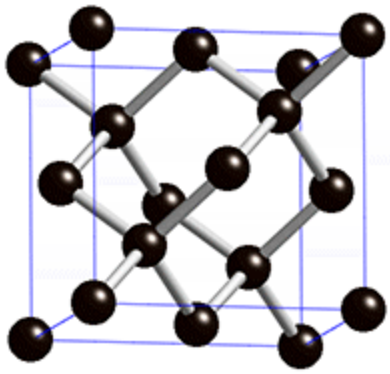


Figure 11.8.2: Rotating model of diamond cubic. (CC0; H.K.D.H. Bhadeshia via Wikipedia)

Notice that diamond is a network solid. The entire solid is an "endless" repetition of carbon atoms bonded to each other by covalent bonds. (In the display at the right, the structure is truncated to fit in the display area.)

Questions to consider

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in diamond?
- The diamond structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- Diamond are renowned for its hardness. Explain why this property is expected on the basis of the structure of diamond.

Graphite

The most stable form of carbon is graphite. Graphite consists of sheets of carbon atoms covalently bonded together. These sheets are then stacked to form graphite. Figure 11.8.3 shows a ball-and-stick representation of graphite with sheets that extended "indefinitely" in the xy plane, but the structure has been truncated for display purposed. Graphite may also be regarded as a network solid, even though there is no bonding in the z direction. Each layer, however, is an "endless" bonded network of carbon atoms.

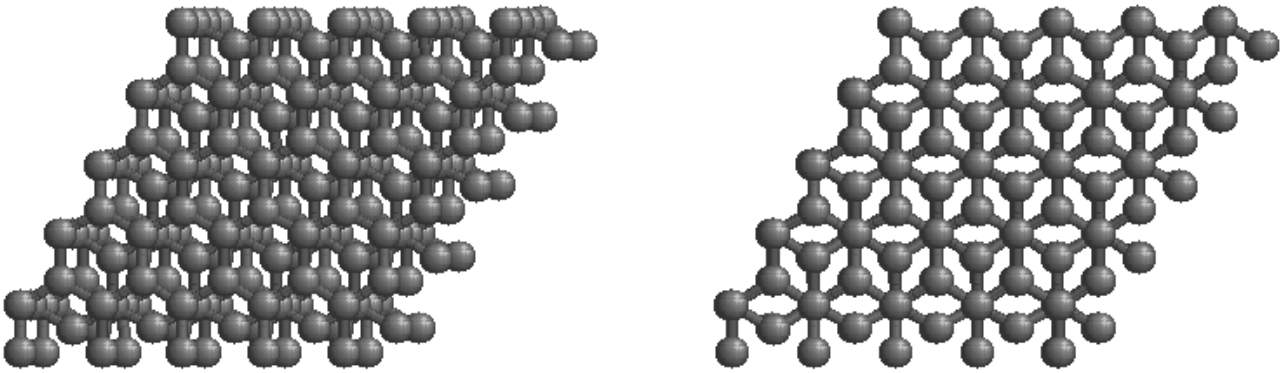


Figure 11.8.3: Animation of a rotating graphite structure. This is a stereogram and can be viewed in 3D if a viewer's eyes are crossed slightly to overlap the two panels. Images used with permission from Wikipedia.

Questions to consider

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in graphite?
- The a layer of the graphite structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- What force holds the carbon sheets together in graphite?
- Graphite is very slippery and is often used in lubricants. Explain why this property is expected on the basis of the structure of graphite.
- The slipperiness of graphite is enhanced by the introduction of impurities. Where would such impurities be located and why would they make graphite a better lubricant?

Fullerenes

Until the mid 1980's, pure carbon was thought to exist in two forms: graphite and diamond. The discovery of C_{60} molecules in interstellar dust in 1985 added a third form to this list. The existence of C_{60}, which resembles a soccer ball, had been hypothesized by theoreticians for many years. In the late 1980's synthetic methods were developed for the synthesis of C_{60}, and the ready availability of this form of carbon led to extensive research into its properties.

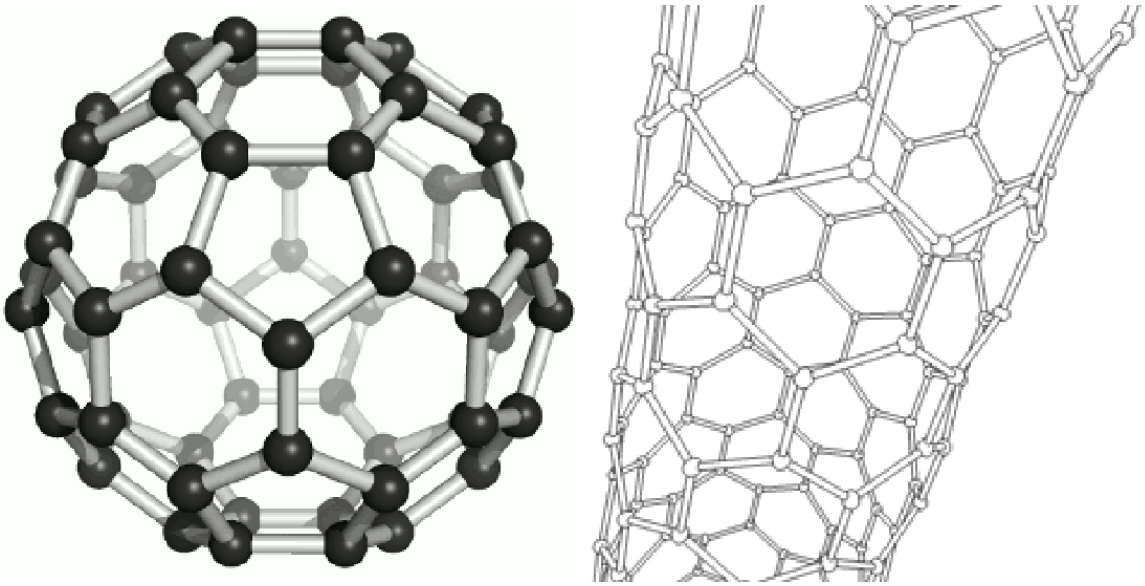


Figure 11.8.4: Example of fullerenes: a buckyball (C_{60} on left and an extended bucktube. Images used with permission from Wikipedia.

The C_{60} molecule (Figure 11.8.4; left), is called buckminsterfullerene, though the shorter name fullerene is often used. The name is a tribute to the American architect R. Buckminster Fuller, who is famous for designing and constructing geodesic domes which bear a close similarity to the structure of C_{60}. As is evident from the display, C_{60} is a sphere composed of six-member and five-member carbon rings. These balls are sometimes fondly referred to as "Bucky balls". It should be noted that fullerenes are an entire class of pure carbon compounds rather than a single compound. A distorted sphere containing more than 60 carbon atoms have also been found, and it is also possible to create long tubes (Figure 11.8.4; right). All of these substances are pure carbon.

Questions to Consider

- What is the bonding geometry around each carbon? (Note that this geometry is distorted in C_{60}.)
- What is the hybridization of carbon in fullerene?
- A single crystal of C60 falls into which class of crystalline solids?
- It has been hypothesized that C60 would make a good lubricant. Why might C60 make a good lubricant?

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 11.8.5. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials.

Metals are characterized by their ability to reflect light, called luster, their high electrical and thermal conductivity, their high heat capacity, and their malleability and ductility. Every lattice point in a pure metallic element is occupied by an atom of the same metal. The packing efficiency in metallic crystals tends to be high, so the resulting metallic solids are dense, with each atom having as many as 12 nearest neighbors.

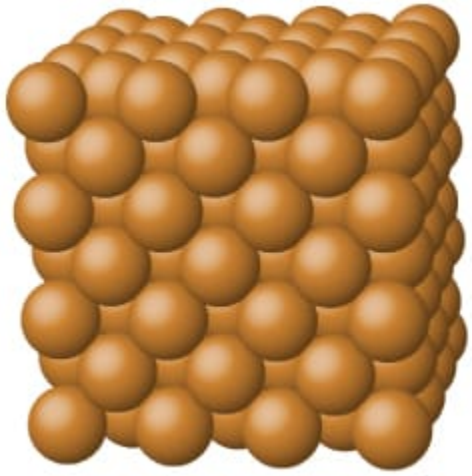


Figure 11.8.5: Copper is a metallic solid. (CC BY 4.0; OpenStax).

Bonding in metallic solids is quite different from the bonding in the other kinds of solids we have discussed. Because all the atoms are the same, there can be no ionic bonding, yet metals always contain too few electrons or valence orbitals to form covalent bonds with each of their neighbors. Instead, the valence electrons are delocalized throughout the crystal, providing a strong cohesive force that holds the metal atoms together.

Valence electrons in a metallic solid are delocalized, providing a strong cohesive force that holds the atoms together.

The strength of metallic bonds varies dramatically. For example, cesium melts at 28.4°C, and mercury is a liquid at room temperature, whereas tungsten melts at 3680°C. Metallic bonds tend to be weakest for elements that have nearly empty (as in

Cs) or nearly full (Hg) valence subshells, and strongest for elements with approximately half-filled valence shells (as in W). As a result, the melting points of the metals increase to a maximum around group 6 and then decrease again from left to right across the d block. Other properties related to the strength of metallic bonds, such as enthalpies of fusion, boiling points, and hardness, have similar periodic trends.

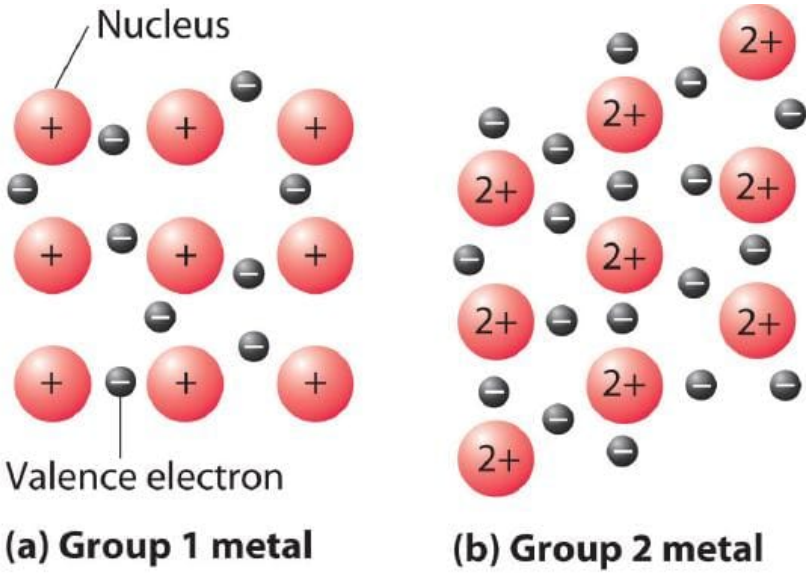


Figure 11.8.6: The Electron-Sea Model of Bonding in Metals. Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a "sea" of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting point.

A somewhat oversimplified way to describe the bonding in a metallic crystal is to depict the crystal as consisting of positively charged nuclei in an electron sea (Figure 11.8.6). In this model, the valence electrons are not tightly bound to any one atom but are distributed uniformly throughout the structure. Very little energy is needed to remove electrons from a solid metal because they are not bound to a single nucleus. When an electrical potential is applied, the electrons can migrate through the solid toward the positive electrode, thus producing high electrical conductivity. The ease with which metals can be deformed under pressure is attributed to the ability of the metal ions to change positions within the electron sea without breaking any specific bonds. The transfer of energy through the solid by successive collisions between the metal ions also explains the high thermal conductivity of metals. This model does not, however, explain many of the other properties of metals, such as their metallic luster and the observed trends in bond strength as reflected in melting points or enthalpies of fusion. Some general properties of the four major classes of solids are summarized in Table 11.8.2.

Table 11.8.2: Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous
***Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.**			

The general order of increasing strength of interactions in a solid is:

molecular solids < ionic solids ≈ metallic solids < covalent solids

Example 11.8.1

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

A. Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.
B. Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

A Germanium lies in the p block just under Si, along the diagonal line of semimetallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a covalent solid. RbI contains a metal from group 1 and a nonmetal from group 17, so it is an ionic solid containing Rb^+ and I^- ions. The compound C6(CH3)6 is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form a molecular solid with no covalent bonds between them. Zn is a d-block element, so it is a metallic solid.

B Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is $C_6(CH_3)_6$ < Zn ~ RbI < Ge. The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

Exercise 11.8.1

Classify C_{60}, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer available at the end of this section.

Summary

The major types of solids are ionic, molecular, covalent, and metallic. Ionic solids consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to have high melting points and are rather hard. Molecular solids are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. As a result, they tend to be rather soft and have low melting points, which depend on their molecular structure. Covalent solids consist of two- or three-dimensional networks of atoms held together by covalent bonds; they tend to be very hard and have high melting points. Metallic solids have unusual properties: in addition to having high thermal and electrical conductivity and being malleable and ductile, they exhibit luster, a shiny surface that reflects light. An alloy is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (substitutional alloys), by inserting smaller atoms into holes in the metal lattice (interstitial alloys), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form intermetallic compounds with unique properties.

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Answers

Exercise 11.8.1

C_{60} (molecular) < AgZn (metallic) ~ $BaBr_2$ (ionic) < GaAs (covalent). The actual melting points are C60, about 300°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

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11.E: Liquids and Intermolecular Forces (Exercises)

11.1: A Molecular Comparison of Gases, Liquids, and Solids

Q11.1.1

A liquid, unlike a gas, is virtually *incompressible*. Explain what this means using macroscopic and microscopic descriptions. What general physical properties do liquids share with solids? What properties do liquids share with gases?

Q11.1.2

Using a kinetic molecular approach, discuss the differences and similarities between liquids and gases with regard to

a. thermal expansion.
b. fluidity.
c. diffusion.

Q11.1.3

How must the ideal gas law be altered to apply the kinetic molecular theory of gases to liquids? Explain.

Q11.1.4

Why are the root mean square speeds of molecules in liquids less than the root mean square speeds of molecules in gases?

11.2: Intermolecular Forces

Conceptual Problems

Q11.2.1

What is the main difference between intramolecular interactions and intermolecular interactions? Which is typically stronger? How are changes of state affected by these different kinds of interactions?

Q11.2.2

Describe the three major kinds of intermolecular interactions discussed in this chapter and their major features. The hydrogen bond is actually an example of one of the other two types of interaction. Identify the kind of interaction that includes hydrogen bonds and explain why hydrogen bonds fall into this category.

Q11.2.3

Which are stronger—dipole–dipole interactions or London dispersion forces? Which are likely to be more important in a molecule with heavy atoms? Explain your answers.

Q11.2.4

Explain why hydrogen bonds are unusually strong compared to other dipole–dipole interactions. How does the strength of hydrogen bonds compare with the strength of covalent bonds?

Q11.2.5

Liquid water is essential for life as we know it, but based on its molecular mass, water should be a gas under standard conditions. Why is water a liquid rather than a gas under standard conditions?

Q11.2.6

Describe the effect of polarity, molecular mass, and hydrogen bonding on the melting point and boiling point of a substance.

Q11.2.7

Why are intermolecular interactions more important for liquids and solids than for gases? Under what conditions must these interactions be considered for gases?

Q11.2.8

Using acetic acid as an example, illustrate both attractive and repulsive intermolecular interactions. How does the boiling point of a substance depend on the magnitude of the repulsive intermolecular interactions?

Q11.2.9

In group 17, elemental fluorine and chlorine are gases, whereas bromine is a liquid and iodine is a solid. Why?

Q11.2.10

The boiling points of the anhydrous hydrogen halides are as follows: HF, 19°C; HCl, −85°C; HBr, −67°C; and HI, −34°C. Explain any trends in the data, as well as any deviations from that trend.

Q11.2.11

Identify the most important intermolecular interaction in each of the following.

a. SO_2
b. HF
c. CO_2
d. CCl_4
e. CH_2Cl_2

Q11.2.12

Identify the most important intermolecular interaction in each of the following.

a. LiF
b. I_2
c. ICl
d. NH_3
e. NH_2Cl

Q11.2.13

Would you expect London dispersion forces to be more important for Xe or Ne? Why? (The atomic radius of Ne is 38 pm, whereas that of Xe is 108 pm.)

Q11.2.14

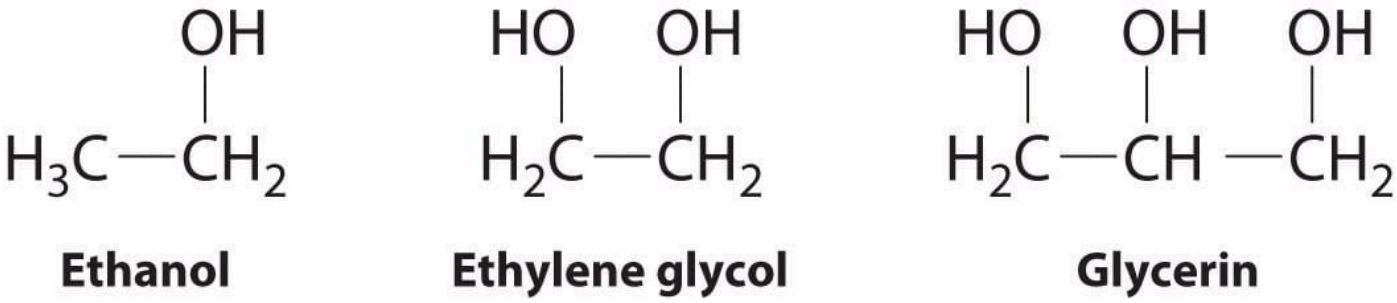
Arrange Kr, Cl_2, H_2, N_2, Ne, and O_2 in order of increasing polarizability. Explain your reasoning.

Q11.2.15

Both water and methanol have anomalously high boiling points due to hydrogen bonding, but the boiling point of water is greater than that of methanol despite its lower molecular mass. Why? Draw the structures of these two compounds, including any lone pairs, and indicate potential hydrogen bonds.

Q11.2.16

The structures of ethanol, ethylene glycol, and glycerin are as follows:



Ethanol **Ethylene glycol** **Glycerin**

Arrange these compounds in order of increasing boiling point. Explain your rationale.

Q11.2.17

Do you expect the boiling point of H_2S to be higher or lower than that of H_2O? Justify your answer.

Q11.2.18

Ammonia (NH_3), methylamine (CH_3NH_2), and ethylamine ($CH_3CH_2NH_2$) are gases at room temperature, while propylamine ($CH_3CH_2CH_2NH_2$) is a liquid at room temperature. Explain these observations.

Q11.2.19

Why is it not advisable to freeze a sealed glass bottle that is completely filled with water? Use both macroscopic and microscopic models to explain your answer. Is a similar consideration required for a bottle containing pure ethanol? Why or why not?

Q11.2.20

Which compound in the following pairs will have the higher boiling point? Explain your reasoning.

- NH_3 or PH_3
- ethylene glycol ($HOCH_2CH_2OH$) or ethanol
- 2,2-dimethylpropanol [$CH_3C(CH_3)_2CH_2OH$] or *n*-butanol ($CH_3CH_2CH_2CH_2OH$)

Q11.2.21

Some recipes call for vigorous boiling, while others call for gentle simmering. What is the difference in the temperature of the cooking liquid between boiling and simmering? What is the difference in energy input?

Q11.2.22

Use the melting of a metal such as lead to explain the process of melting in terms of what is happening at the molecular level. As a piece of lead melts, the temperature of the metal remains constant, even though energy is being added continuously. Why?

Q11.2.23

How does the O–H distance in a hydrogen bond in liquid water compare with the O–H distance in the covalent O–H bond in the H_2O molecule? What effect does this have on the structure and density of ice?

Q11.2.24

Explain why the hydrogen bonds in liquid HF are stronger than the corresponding intermolecular H · · · I interactions in liquid HI.

a. In which substance are the individual hydrogen bonds stronger: HF or H_2O? Explain your reasoning.
b. For which substance will hydrogen bonding have the greater effect on the boiling point: HF or H_2O? Explain your reasoning.

Answers

2.
3.
4.
5. Water is a liquid under standard conditions because of its unique ability to form four strong hydrogen bonds per molecule.
6.
7.
8.
9. As the atomic mass of the halogens increases, so does the number of electrons and the average distance of those electrons from the nucleus. Larger atoms with more electrons are more easily polarized than smaller atoms, and the increase in polarizability with atomic number increases the strength of London dispersion forces. These intermolecular interactions are strong enough to favor the condensed states for bromine and iodine under normal conditions of temperature and pressure.
10.
11.
    1. The V-shaped SO_2 molecule has a large dipole moment due to the polar S=O bonds, so dipole–dipole interactions will be most important.
    2. The H–F bond is highly polar, and the fluorine atom has three lone pairs of electrons to act as hydrogen bond acceptors; hydrogen bonding will be most important.
    3. Although the C=O bonds are polar, this linear molecule has no net dipole moment; hence, London dispersion forces are most important.
    4. This is a symmetrical molecule that has no net dipole moment, and the Cl atoms are relatively polarizable; thus, London dispersion forces will dominate.
    5. This molecule has a small dipole moment, as well as polarizable Cl atoms. In such a case, dipole–dipole interactions and London dispersion forces are often comparable in magnitude.
12.
13.
14.
15. Water has two polar O–H bonds with H atoms that can act as hydrogen bond donors, plus two lone pairs of electrons that can act as hydrogen bond acceptors, giving a net of *four* hydrogen bonds per H_2O molecule. Although methanol also has two lone pairs of electrons on oxygen that can act as hydrogen bond acceptors, it only has one O–H bond with an H atom that can act as a hydrogen bond donor. Consequently, methanol can only form *two* hydrogen bonds per molecule on average, versus four for water. Hydrogen bonding therefore has a much greater effect on the boiling point of water.
16.
17.
18.
19.
20.
21. Vigorous boiling causes more water molecule to escape into the vapor phase, but does not affect the temperature of the liquid. Vigorous boiling requires a higher energy input than does gentle simmering.

11.3: Some Properties of Liquids

Conceptual Problems

1. Why is a water droplet round?

2. How is the environment of molecules on the surface of a liquid droplet different from that of molecules in the interior of the droplet? How is this difference related to the concept of surface tension?

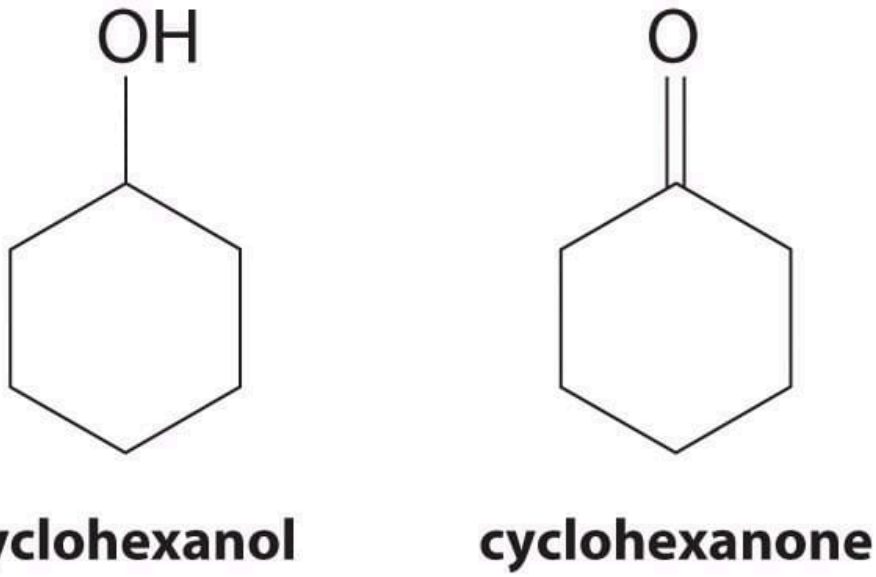
3. Explain the role of intermolecular and intramolecular forces in surface tension.

4. A mosquito is able to walk across water without sinking, but if a few drops of detergent are added to the water, the insect will sink. Why?

5. Explain how soaps or surfactants decrease the surface tension of a liquid. How does the meniscus of an aqueous solution in a capillary change if a surfactant is added? Illustrate your answer with a diagram.

6. Of CH_2Cl_2, hexane, and ethanol, which has the lowest viscosity? Which has the highest surface tension? Explain your reasoning in each case.

7. At 25°C, cyclohexanol has a surface tension of 32.92 mN/m^2, whereas the surface tension of cyclohexanone, which is very similar chemically, is only 25.45 mN/m^2. Why is the surface tension of cyclohexanone so much less than that of cyclohexanol?



8. What is the relationship between

    1. surface tension and temperature?
    2. viscosity and temperature?

    Explain your answers in terms of a microscopic picture.

9. What two opposing forces are responsible for capillary action? How do these forces determine the shape of the meniscus?

10. Which of the following liquids will have a concave meniscus in a glass capillary? Explain your reasoning.

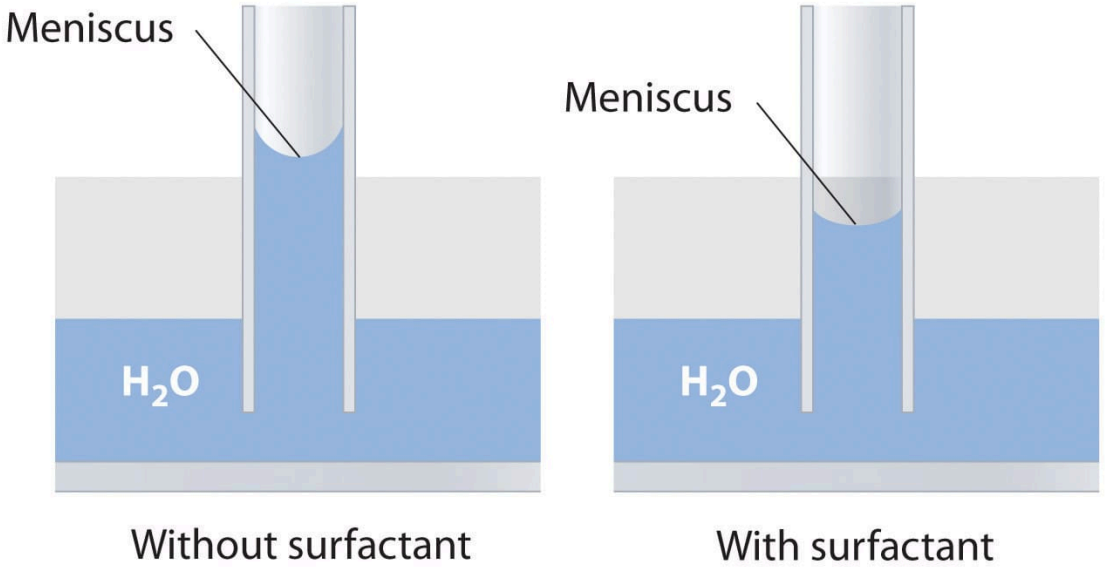
    1. pentane
    2. diethylene glycol ($HOCH_2CH_2OCH_2CH_2OH$)
    3. carbon tetrachloride

11. How does viscosity depend on molecular shape? What molecular features make liquids highly viscous?

Conceptual Answers

4.

5. Adding a soap or a surfactant to water disrupts the attractive intermolecular interactions between water molecules, thereby decreasing the surface tension. Because water is a polar molecule, one would expect that a soap or a surfactant would also disrupt the attractive interactions responsible for adhesion of water to the surface of a glass capillary. As shown in the sketch, this would decrease the height of the water column inside the capillary, as well as making the meniscus less concave.



6.
7. As the structures indicate, cyclohexanol is a polar substance that can engage in hydrogen bonding, much like methanol or ethanol; consequently, it is expected to have a higher surface tension due to stronger intermolecular interactions.
8.
9. Cohesive forces are the intermolecular forces that hold the molecules of the liquid together, while adhesive forces are the attractive forces between the molecules of the liquid and the walls of the capillary. If the adhesive forces are stronger than the cohesive forces, the liquid is pulled up into the capillary and the meniscus is concave. Conversely, if the cohesive forces are stronger than the adhesive forces, the level of the liquid inside the capillary will be lower than the level outside the capillary, and the meniscus will be convex.
10.
11. Viscous substances often consist of molecules that are much longer than they are wide and whose structures are often rather flexible. As a result, the molecules tend to become tangled with one another (much like overcooked spaghetti), which decreases the rate at which they can move through the liquid.

Numerical Problems

1. The viscosities of five liquids at 25°C are given in the following table. Explain the observed trends in viscosity.

Compound	Molecular Formula	Viscosity (mPa•s)
benzene	C_6H_6	0.604
aniline	$C_6H_5NH_2$	3.847
1,2-dichloroethane	$C_2H_4Cl_2$	0.779
heptane	C_7H_{16}	0.357
1-heptanol	$C_7H_{15}OH$	5.810

- The following table gives values for the viscosity, boiling point, and surface tension of four substances. Examine these data carefully to see whether the data for each compound are internally consistent and point out any obvious errors or inconsistencies. Explain your reasoning.

Compound	Viscosity (mPa•s at 20°C)	Boiling Point (°C)	Surface Tension (dyn/cm at 25°C)
A	0.41	61	27.16
B	0.55	65	22.55

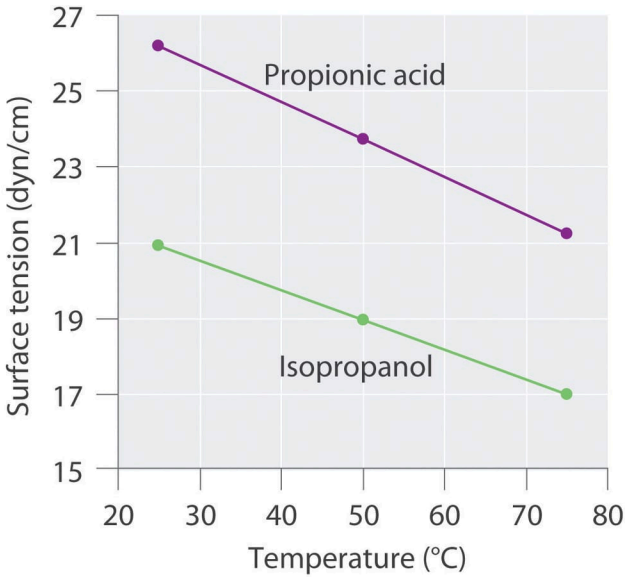
Compound	Viscosity (mPa•s at 20°C)	Boiling Point (°C)	Surface Tension (dyn/cm at 25°C)
C	0.92	105	36.76
D	0.59	110	28.53

- Surface tension data (in dyn/cm) for propanoic acid ($C_3H_6O_2$), and 2-propanol (C_3H_8O), as a function of temperature, are given in the following table. Plot the data for each compound and explain the differences between the two graphs. Based on these data, which molecule is more polar?

Compound	25°C	50°C	75°C
propanoic acid	26.20	23.72	21.23
2-propanol	20.93	18.96	16.98

Numerical Answer

3. The plots of surface tension versus temperature for propionic acid and isopropanol have essentially the same slope, but at all temperatures the surface tension of propionic acid is about 30% greater than for isopropanol. Because surface tension is a measure of the cohesive forces in a liquid, these data suggest that the cohesive forces for propionic acid are significantly greater than for isopropanol. Both substances consist of polar molecules with similar molecular masses, and the most important intermolecular interactions are likely to be dipole–dipole interactions. Consequently, these data suggest that propionic acid is more polar than isopropanol.



11.4: Phase Changes

Conceptual Problems

1. In extremely cold climates, snow can disappear with no evidence of its melting. How can this happen? What change(s) in state are taking place? Would you expect this phenomenon to be more common at high or low altitudes? Explain your answer.

2. Why do car manufacturers recommend that an automobile should not be left standing in subzero temperatures if its radiator contains only water? Car manufacturers also warn car owners that they should check the fluid level in a radiator only when the engine is cool. What is the basis for this warning? What is likely to happen if it is ignored?

3. Use Hess's law and a thermochemical cycle to show that, for any solid, the enthalpy of sublimation is equal to the sum of the enthalpy of fusion of the solid and the enthalpy of vaporization of the resulting liquid.

4. Three distinct processes occur when an ice cube at –10°C is used to cool a glass of water at 20°C. What are they? Which causes the greatest temperature change in the water?

5. When frost forms on a piece of glass, crystals of ice are deposited from water vapor in the air. How is this process related to sublimation? Describe the energy changes that take place as the water vapor is converted to frost.

6. What phase changes are involved in each process? Which processes are exothermic, and which are endothermic?

    1. ice melting
    2. distillation
    3. condensation forming on a window
    4. the use of dry ice to create a cloud for a theatrical production

7. What phase changes are involved in each process? Which processes are exothermic, and which are endothermic?

    1. evaporation of methanol
    2. crystallization
    3. liquefaction of natural gas
    4. the use of naphthalene crystals to repel moths

8. Why do substances with high enthalpies of fusion tend to have high melting points?

9. Why is the enthalpy of vaporization of a compound invariably much larger than its enthalpy of fusion?

10. What is the opposite of fusion, sublimation, and condensation? Describe the phase change in each pair of opposing processes and state whether each phase change is exothermic or endothermic.

11. Draw a typical heating curve (temperature versus amount of heat added at a constant rate) for conversion of a solid to a liquid and then to a gas. What causes some regions of the plot to have a positive slope? What is happening in the regions of the plot where the curve is horizontal, meaning that the temperature does not change even though heat is being added?

12. If you know the mass of a sample of a substance, how could you use a heating curve to calculate the specific heat of the substance, as well as the change in enthalpy associated with a phase change?

13. Draw the heating curve for a liquid that has been superheated. How does this differ from a normal heating curve for a liquid? Draw the cooling curve for a liquid that has been supercooled. How does this differ from a normal cooling curve for a liquid?

Conceptual Answers

1. When snow disappears without melting, it must be subliming directly from the solid state to the vapor state. The rate at which this will occur depends solely on the partial pressure of water, not on the total pressure due to other gases. Consequently, altitude (and changes in atmospheric pressure) will not affect the rate of sublimation directly.
2.

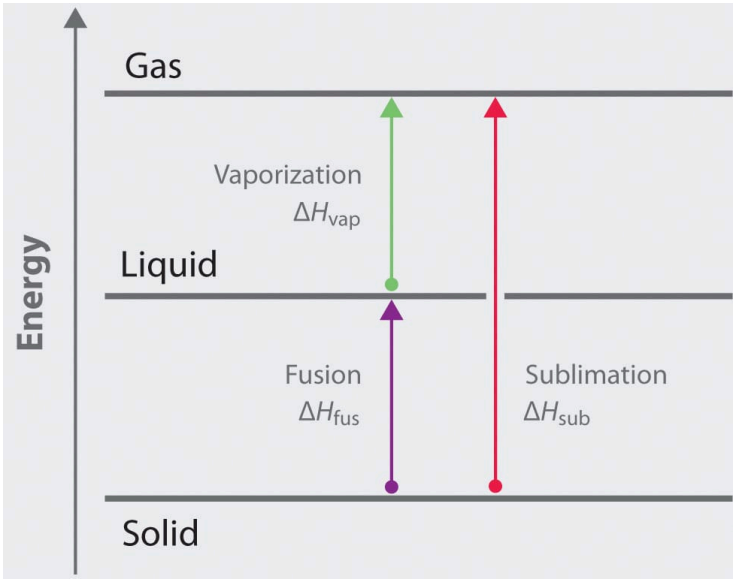
3 The general equations and enthalpy changes for the changes of state involved in converting a solid to a gas are:

$$\text{solid} \rightarrow \text{liquid} : \Delta H_{fus} \tag{11.E.1}$$

$$\text{liquid} \rightarrow \text{gas} : \Delta H_{vap} \tag{11.E.2}$$

$$\text{solid} \rightarrow \text{gas} : \Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{11.E.3}$$

The relationship between these enthalpy changes is shown schematically in the thermochemical cycle below:



4.

5. The formation of frost on a surface is an example of deposition, which is the reverse of sublimation. The change in enthalpy for deposition is equal in magnitude, but opposite in sign, to ΔH_{sub}, which is a positive number: $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$.

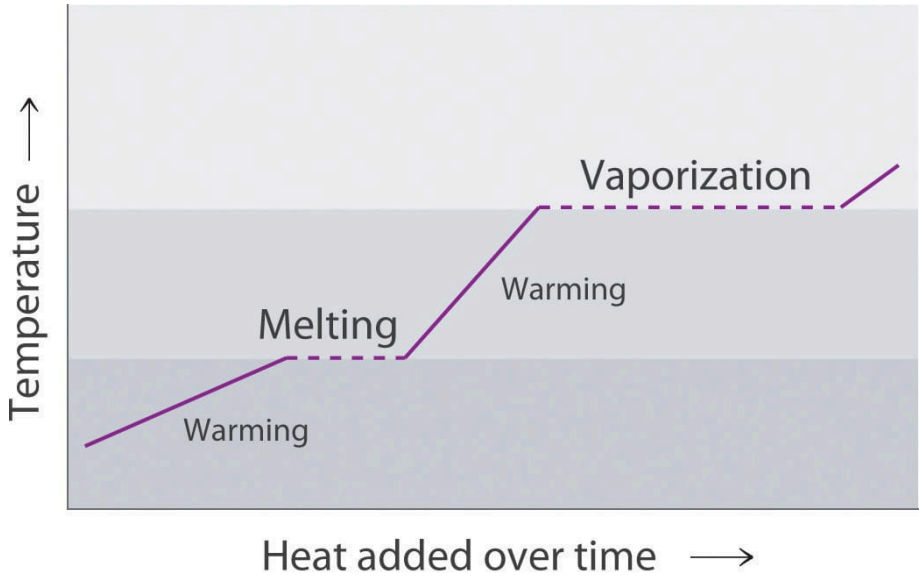
6.

7.
   1. liquid + heat → vapor: endothermic
   2. liquid → solid + heat: exothermic
   3. gas → liquid + heat: exothermic
   4. solid + heat → vapor: endothermic

8.

9. The enthalpy of vaporization is larger than the enthalpy of fusion because vaporization requires the addition of enough energy to disrupt all intermolecular interactions and create a gas in which the molecules move essentially independently. In contrast, fusion requires much less energy, because the intermolecular interactions in a liquid and a solid are similar in magnitude in all condensed phases. Fusion requires only enough energy to overcome the intermolecular interactions that lock molecules in place in a lattice, thereby allowing them to move more freely.

10.

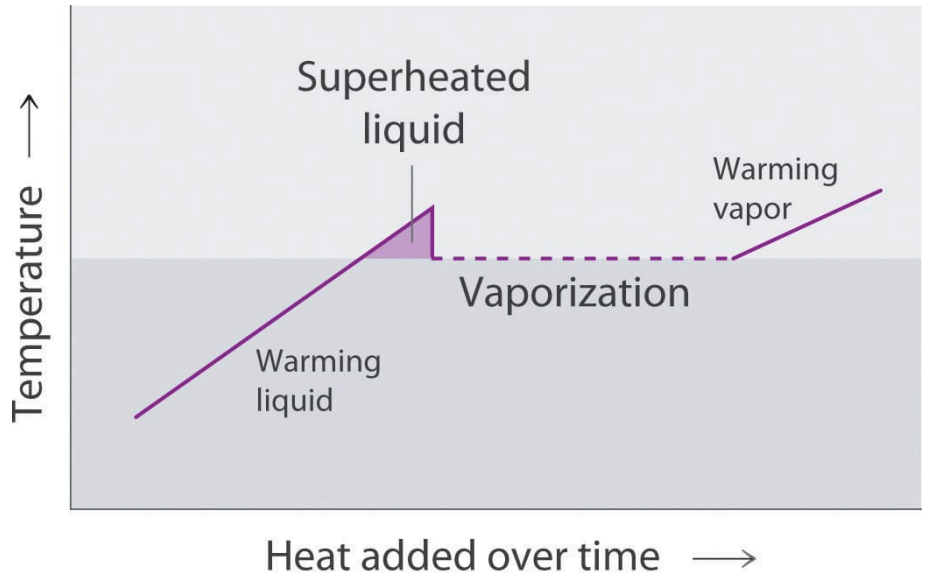


11.

The portions of the curve with a positive slope correspond to heating a single phase, while the horizontal portions of the curve correspond to phase changes. During a phase change, the temperature of the system does not change, because the added heat is melting the solid at its melting point or evaporating the liquid at its boiling point.

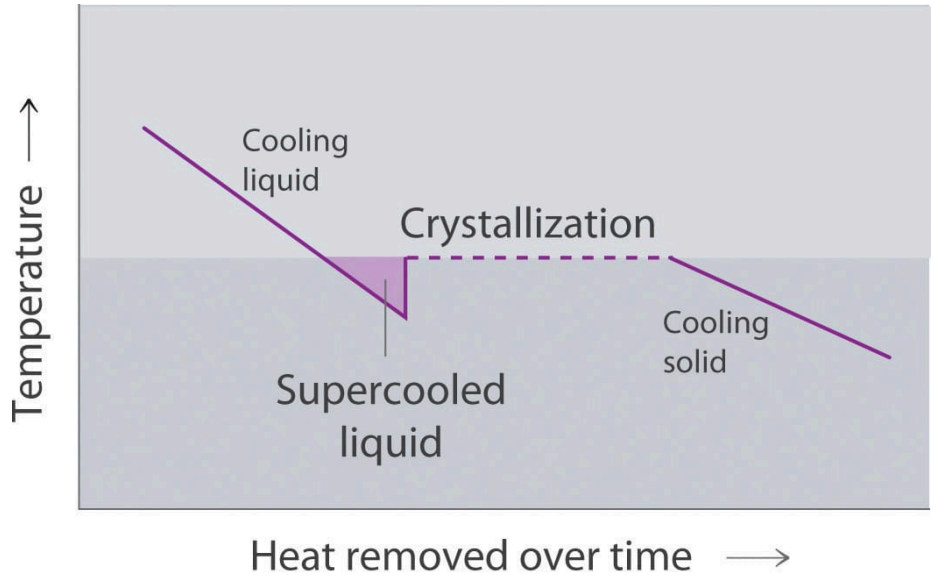
12.

13.



A superheated liquid exists temporarily as liquid with a temperature above the normal boiling point of the liquid. When a supercooled liquid boils, the temperature drops as the liquid is converted to vapor.

Conversely, a supercooled liquid exists temporarily as a liquid with a temperature lower than the normal melting point of the solid. As shown below, when a supercooled liquid crystallizes, the temperature increases as the liquid is converted to a solid.



Numerical Problems

1. The density of oxygen at 1 atm and various temperatures is given in the following table. Plot the data and use your graph to predict the normal boiling point of oxygen.

***T* (K)**	60	70	80	90	100	120	140
***d* (mol/L)**	40.1	38.6	37.2	35.6	0.123	0.102	0.087

2. The density of propane at 1 atm and various temperatures is given in the following table. Plot the data and use your graph to predict the normal boiling point of propane.

T (K)	100	125	150	175	200	225	250	275
d (mol/L)	16.3	15.7	15.0	14.4	13.8	13.2	0.049	0.044

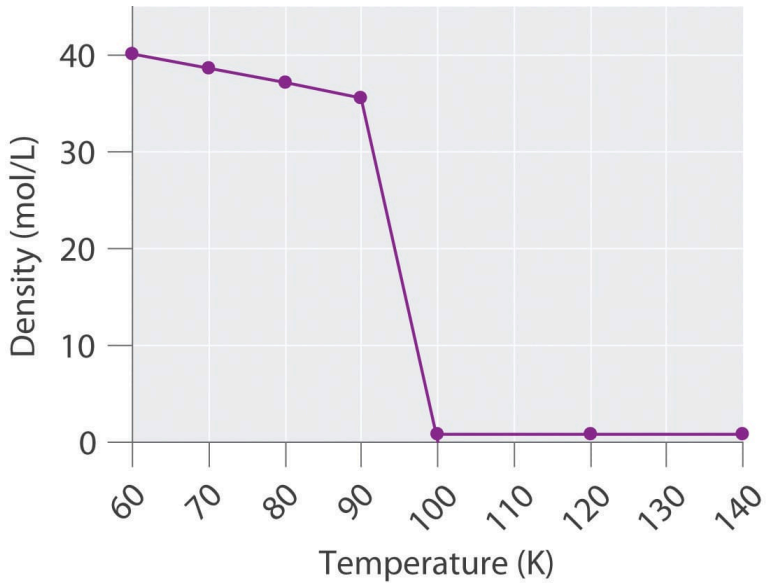
- Draw the cooling curve for a sample of the vapor of a compound that has a melting point of 34°C and a boiling point of 77°C as it is cooled from 100°C to 0°C.
- Propionic acid has a melting point of −20.8°C and a boiling point of 141°C. Draw a heating curve showing the temperature versus time as heat is added at a constant rate to show the behavior of a sample of propionic acid as it is heated from −50°C to its boiling point. What happens above 141°C?
- A 0.542 g sample of I_2 requires 96.1 J of energy to be converted to vapor. What is the enthalpy of sublimation of I_2?
- A 2.0 L sample of gas at 210°C and 0.762 atm condenses to give 1.20 mL of liquid, and 476 J of heat is released during the process. What is the enthalpy of vaporization of the compound?
- One fuel used for jet engines and rockets is aluminum borohydride [$Al(BH_4)_3$], a liquid that readily reacts with water to produce hydrogen. The liquid has a boiling point of 44.5°C. How much energy is needed to vaporize 1.0 kg of aluminum borohydride at 20°C, given a ΔH_{vap} of 30 kJ/mol and a molar heat capacity (C_p) of 194.6 J/(mol•K)?
- How much energy is released when freezing 100.0 g of dimethyl disulfide ($C_2H_6S_2$) initially at 20°C? Use the following information: melting point = −84.7°C, ΔH_{fus} = 9.19 kJ/mol, C_p = 118.1 J/(mol•K).

The following four problems use the following information (the subscript p indicates measurements taken at constant pressure): $\Delta H_{fus}(H_2O)$ = 6.01 kJ/mol, $\Delta H_{vap}(H_2O)$ = 40.66 kJ/mol, $C_{p(s)}$(crystalline H_2O) = 38.02 J/(mol•K), $C_{p(l)}$(liquid H_2O) = 75.35 J/(mol•K), and $C_{p(g)}$(H_2O gas) = 33.60 J/(mol•K).

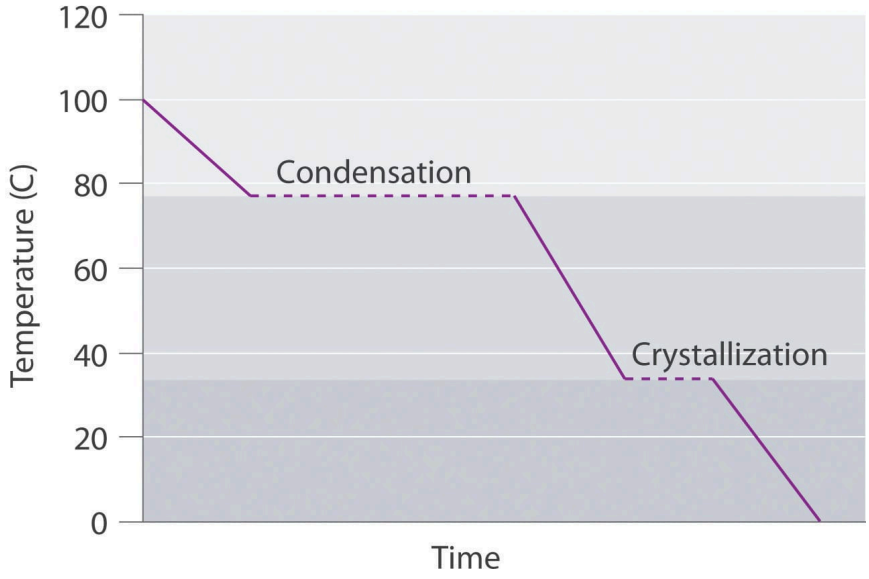
9. How much heat is released in the conversion of 1.00 L of steam at 21.9 atm and 200°C to ice at −6.0°C and 1 atm?
10. How much heat must be applied to convert a 1.00 g piece of ice at −10°C to steam at 120°C?
11. How many grams of boiling water must be added to a glass with 25.0 g of ice at −3°C to obtain a liquid with a temperature of 45°C?
12. How many grams of ice at −5.0°C must be added to 150.0 g of water at 22°C to give a final temperature of 15°C?

Numerical Answers

1.



The transition from a liquid to a gaseous phase is accompanied by a drastic decrease in density. According to the data in the table and the plot, the boiling point of liquid oxygen is between 90 and 100 K (actually 90.2 K).

2. 

3.
4.
5. 45.0 kJ/mol
6.
7. 488 kJ
8.
9. 32.6 kJ
10.
11. 57 g

11.5: Vapor Pressure

Conceptual Problems

1. What is the relationship between the boiling point, vapor pressure, and temperature of a substance and atmospheric pressure?

2. What is the difference between a volatile liquid and a nonvolatile liquid? Suppose that two liquid substances have the same molecular mass, but one is volatile and the other is nonvolatile. What differences in the molecular structures of the two substances could account for the differences in volatility?

3. An “old wives’ tale” states that applying ethanol to the wrists of a child with a very high fever will help to reduce the fever because blood vessels in the wrists are close to the skin. Is there a scientific basis for this recommendation? Would water be as effective as ethanol?

4. Why is the air over a strip of grass significantly cooler than the air over a sandy beach only a few feet away?

5. If gasoline is allowed to sit in an open container, it often feels much colder than the surrounding air. Explain this observation. Describe the flow of heat into or out of the system, as well as any transfer of mass that occurs. Would the temperature of a sealed can of gasoline be higher, lower, or the same as that of the open can? Explain your answer.

6. What is the relationship between the vapor pressure of a liquid and

    1. its temperature?
    2. the surface area of the liquid?
    3. the pressure of other gases on the liquid?
    4. its viscosity?

7. At 25°C, benzene has a vapor pressure of 12.5 kPa, whereas the vapor pressure of acetic acid is 2.1 kPa. Which is more volatile? Based on the intermolecular interactions in the two liquids, explain why acetic acid has the lower vapor pressure.

Numerical Problems

1. Acetylene (C_2H_2), which is used for industrial welding, is transported in pressurized cylinders. Its vapor pressure at various temperatures is given in the following table. Plot the data and use your graph to estimate the vapor pressure of acetylene at 293 K. Then use your graph to determine the value of ΔH_{vap} for acetylene. How much energy is required to vaporize 2.00 g of acetylene at 250 K?

***T* (K)**	145	155	175	200	225	250	300
***P* (mmHg)**	1.3	7.8	32.2	190	579	1370	5093

2. The following table gives the vapor pressure of water at various temperatures. Plot the data and use your graph to estimate the vapor pressure of water at 25°C and at 75°C. What is the vapor pressure of water at 110°C? Use these data to determine the value of ΔH_{vap} for water.

***T* (°C)**	0	10	30	50	60	80	100
***P* (mmHg)**	4.6	9.2	31.8	92.6	150	355	760

3. The ΔH_{vap} of carbon tetrachloride is 29.8 kJ/mol, and its normal boiling point is 76.8°C. What is its boiling point at 0.100 atm?

4. The normal boiling point of sodium is 883°C. If ΔH_{vap} is 97.4 kJ/mol, what is the vapor pressure (in millimeters of mercury) of liquid sodium at 300°C?

5. An unknown liquid has a vapor pressure of 0.860 atm at 63.7°C and a vapor pressure of 0.330 atm at 35.1°C. Use the data in Table 11.6 in Section 11.5 to identify the liquid.

6. An unknown liquid has a boiling point of 75.8°C at 0.910 atm and a boiling point of 57.2°C at 0.430 atm. Use the data in Table 11.6 in Section 11.5 to identify the liquid.

7. If the vapor pressure of a liquid is 0.850 atm at 20°C and 0.897 atm at 25°C, what is the normal boiling point of the liquid?

8. If the vapor pressure of a liquid is 0.799 atm at 99.0°C and 0.842 atm at 111°C, what is the normal boiling point of the liquid?

9. The vapor pressure of liquid SO_2 is 33.4 torr at −63.4°C and 100.0 torr at −47.7 K.

    1. What is the ΔH_{vap} of SO_2?
    2. What is its vapor pressure at −24.5 K?
    3. At what temperature is the vapor pressure equal to 220 torr?

10. The vapor pressure of CO_2 at various temperatures is given in the following table:

T **(°C)**	−120	−110	−100	−90
P **(torr)**	9.81	34.63	104.81	279.5

    1. What is ΔH_{vap} over this temperature range?
    2. What is the vapor pressure of CO_2 at −70°C?
    3. At what temperature does CO_2 have a vapor pressure of 310 torr?

Numerical Answers

1.

vapor pressure at 273 K is 3050 mmHg; ΔH_{vap} = 18.7 kJ/mol, 1.44 kJ

2.
3. 12.5°C
4.
5. ΔH_{vap} = 28.9 kJ/mol, *n*-hexane
6.
7. ΔH_{vap} = 7.81 kJ/mol, 36°C

11.6: Phase Diagrams

Conceptual Problems

1. A phase diagram is a graphic representation of the stable phase of a substance at any combination of temperature and pressure. What do the lines separating different regions in a phase diagram indicate? What information does the slope of a line in a phase diagram convey about the physical properties of the phases it separates? Can a phase diagram have more than one point where three lines intersect?
2. If the slope of the line corresponding to the solid/liquid boundary in the phase diagram of water were positive rather than negative, what would be the effect on aquatic life during periods of subzero temperatures? Explain your answer.

Conceptual Answer

1. The lines in a phase diagram represent boundaries between different phases; at any combination of temperature and pressure that lies on a line, two phases are in equilibrium. It is physically impossible for more than three phases to coexist at any combination of temperature and pressure, but in principle there can be more than one triple point in a phase diagram. The slope of the line separating two phases depends upon their relative densities. For example, if the solid–liquid line slopes up and to the *right*, the liquid is less dense than the solid, while if it slopes up and to the *left*, the liquid is denser than the solid.

Numerical Problems

1. Naphthalene ($C_{10}H_8$) is the key ingredient in mothballs. It has normal melting and boiling points of 81°C and 218°C, respectively. The triple point of naphthalene is 80°C at 1000 Pa. Use these data to construct a phase diagram for naphthalene and label all the regions of your diagram.
2. Argon is an inert gas used in welding. It has normal boiling and freezing points of 87.3 K and 83.8 K, respectively. The triple point of argon is 83.8 K at 0.68 atm. Use these data to construct a phase diagram for argon and label all the regions of your diagram.

11.7: Structure of Solids

Conceptual Problems

1. Compare the solid and liquid states in terms of

    a. rigidity of structure.

    b. long-range order.

    c. short-range order.

2. How do amorphous solids differ from crystalline solids in each characteristic? Which of the two types of solid is most similar to a liquid?

    a. rigidity of structure

    b. long-range order

c. short-range order

3. Why is the arrangement of the constituent atoms or molecules more important in determining the properties of a solid than a liquid or a gas?

4. Why are the structures of solids usually described in terms of the positions of the constituent atoms rather than their motion?

5. What physical characteristics distinguish a crystalline solid from an amorphous solid? Describe at least two ways to determine experimentally whether a material is crystalline or amorphous.

6. Explain why each characteristic would or would not favor the formation of an amorphous solid.

a. slow cooling of pure molten material

b. impurities in the liquid from which the solid is formed

c. weak intermolecular attractive forces

7. A student obtained a solid product in a laboratory synthesis. To verify the identity of the solid, she measured its melting point and found that the material melted over a 12°C range. After it had cooled, she measured the melting point of the same sample again and found that this time the solid had a sharp melting point at the temperature that is characteristic of the desired product. Why were the two melting points different? What was responsible for the change in the melting point?

Conceptual Answers II

3. The arrangement of the atoms or molecules is more important in determining the properties of a solid because of the greater persistent long-range order of solids. Gases and liquids cannot readily be described by the spatial arrangement of their components because rapid molecular motion and rearrangement defines many of the properties of liquids and gases.

7. The initial solid contained the desired compound in an amorphous state, as indicated by the wide temperature range over which melting occurred. Slow cooling of the liquid caused it to crystallize, as evidenced by the sharp second melting point observed at the expected temperature.

Conceptual Problems II

1. Why is it valid to represent the structure of a crystalline solid by the structure of its unit cell? What are the most important constraints in selecting a unit cell?
2. All unit cell structures have six sides. Can crystals of a solid have more than six sides? Explain your answer.
3. Explain how the intensive properties of a material are reflected in the unit cell. Are all the properties of a bulk material the same as those of its unit cell? Explain your answer.
4. The experimentally measured density of a bulk material is slightly higher than expected based on the structure of the pure material. Propose two explanations for this observation.
5. The experimentally determined density of a material is lower than expected based on the arrangement of the atoms in the unit cell, the formula mass, and the size of the atoms. What conclusion(s) can you draw about the material?
6. Only one element (polonium) crystallizes with a simple cubic unit cell. Why is polonium the only example of an element with this structure?
7. What is meant by the term coordination number in the structure of a solid? How does the coordination number depend on the structure of the metal?
8. Arrange the three types of cubic unit cells in order of increasing packing efficiency. What is the difference in packing efficiency between the hcp structure and the ccp structure?
9. The structures of many metals depend on pressure and temperature. Which structure—bcc or hcp—would be more likely in a given metal at very high pressures? Explain your reasoning.
10. A metal has two crystalline phases. The transition temperature, the temperature at which one phase is converted to the other, is 95°C at 1 atm and 135°C at 1000 atm. Sketch a phase diagram for this substance. The metal is known to have either a ccp structure or a simple cubic structure. Label the regions in your diagram appropriately and justify your selection for the structure of each phase.

Numerical Problems II

1. Metallic rhodium has an fcc unit cell. How many atoms of rhodium does each unit cell contain?
2. Chromium has a structure with two atoms per unit cell. Is the structure of this metal simple cubic, bcc, fcc, or hcp?
3. The density of nickel is 8.908 g/cm^3. If the metallic radius of nickel is 125 pm, what is the structure of metallic nickel?
4. The density of tungsten is 19.3 g/cm^3. If the metallic radius of tungsten is 139 pm, what is the structure of metallic tungsten?
5. An element has a density of 10.25 g/cm^3 and a metallic radius of 136.3 pm. The metal crystallizes in a bcc lattice. Identify the element.
6. A 21.64 g sample of a nonreactive metal is placed in a flask containing 12.00 mL of water; the final volume is 13.81 mL. If the length of the edge of the unit cell is 387 pm and the metallic radius is 137 pm, determine the packing arrangement and identify the element.
7. A sample of an alkali metal that has a bcc unit cell is found to have a mass of 1.000 g and a volume of 1.0298 cm^3. When the metal reacts with excess water, the reaction produces 539.29 mL of hydrogen gas at 0.980 atm and 23°C. Identify the metal, determine the unit cell dimensions, and give the approximate size of the atom in picometers.
8. A sample of an alkaline earth metal that has a bcc unit cell is found to have a mass 5.000 g and a volume of 1.392 cm^3. Complete reaction with chlorine gas requires 848.3 mL of chlorine gas at 1.050 atm and 25°C. Identify the metal, determine the unit cell dimensions, and give the approximate size of the atom in picometers.
9. Lithium crystallizes in a bcc structure with an edge length of 3.509 Å. Calculate its density. What is the approximate metallic radius of lithium in picometers?
10. Vanadium is used in the manufacture of rust-resistant vanadium steel. It forms bcc crystals with a density of 6.11 g/cm^3 at 18.7°C. What is the length of the edge of the unit cell? What is the approximate metallic radius of the vanadium in picometers?
11. A simple cubic cell contains one metal atom with a metallic radius of 100 pm.
    a. Determine the volume of the atom(s) contained in one unit cell [the volume of a sphere = $(\frac{4}{3})\pi r^3$].
    b. What is the length of one edge of the unit cell? (Hint: there is no empty space between atoms.)
    c. Calculate the volume of the unit cell.
    d. Determine the packing efficiency for this structure.
    e. Use the steps in Problem 11 to calculate the packing efficiency for a bcc unit cell with a metallic radius of 1.00 Å.

Numerical Answers

1. four

3. fcc

5. molybdenum

7. sodium, unit cell edge = 428 pm, r = 185 pm

9. d = 0.5335 g/cm^3, r =151.9 pm

11.8: Bonding in Solids

Conceptual Problems

1. Four vials labeled A–D contain sucrose, zinc, quartz, and sodium chloride, although not necessarily in that order. The following table summarizes the results of the series of analyses you have performed on the contents:

	A	B	C	D
Melting Point	high	high	high	low
Thermal Conductivity	poor	poor	good	poor

	A	B	C	D
Electrical Conductivity in Solid State	moderate	poor	high	poor
Electrical Conductivity in Liquid State	high	poor	high	poor
Hardness	hard	hard	soft	soft
Luster	none	none	high	none

Match each vial with its contents.

2. Do ionic solids generally have higher or lower melting points than molecular solids? Why? Do ionic solids generally have higher or lower melting points than covalent solids? Explain your reasoning.

3. The strength of London dispersion forces in molecular solids tends to increase with molecular mass, causing a smooth increase in melting points. Some molecular solids, however, have significantly lower melting points than predicted by their molecular masses. Why?

4. Suppose you want to synthesize a solid that is both heat resistant and a good electrical conductor. What specific types of bonding and molecular interactions would you want in your starting materials?

5. Explain the differences between an interstitial alloy and a substitutional alloy. Given an alloy in which the identity of one metallic element is known, how could you determine whether it is a substitutional alloy or an interstitial alloy?

6. How are intermetallic compounds different from interstitial alloys or substitutional alloys?

Conceptual Answers

1.

a. NaCl, ionic solid

b. quartz, covalent solid

c. zinc, metal

d. sucrose, molecular solid

5. In a substitutional alloy, the impurity atoms are similar in size and chemical properties to the atoms of the host lattice; consequently, they simply replace some of the metal atoms in the normal lattice and do not greatly perturb the structure and physical properties. In an interstitial alloy, the impurity atoms are generally much smaller, have very different chemical properties, and occupy holes between the larger metal atoms. Because interstitial impurities form covalent bonds to the metal atoms in the host lattice, they tend to have a large effect on the mechanical properties of the metal, making it harder, less ductile, and more brittle. Comparing the mechanical properties of an alloy with those of the parent metal could be used to decide whether the alloy were a substitutional or interstitial alloy.

Numerical Problems

1. Will the melting point of lanthanum(III) oxide be higher or lower than that of ferrous bromide? The relevant ionic radii are as follows: La^{3+}, 104 pm; O^{2-}, 132 pm; Fe^{2+}, 83 pm; and Br^{-}, 196 pm. Explain your reasoning.

2. Draw a graph showing the relationship between the electrical conductivity of metallic silver and temperature.

3. Which has the higher melting point? Explain your reasoning in each case.

a. Os or Hf

b. SnO_2 or ZrO_2

c. Al_2O_3 or SiO_2

4. Draw a graph showing the relationship between the electrical conductivity of a typical semiconductor and temperature.

Numerical Answer

3.

a. Osmium has a higher melting point, due to more valence electrons for metallic bonding.

b. Zirconium oxide has a higher melting point, because it has greater ionic character.

c. Aluminum oxide has a higher melting point, again because it has greater ionic character.

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11.S: Liquids and Intermolecular Forces (Summary)

- intermolecular forces – forces that exist between molecules

11.1: A Molecular Comparison of Gases, Liquids, and Solids

The state of a substance depends on the balance between the kinetic energy of the individual particles (molecules or atoms) and the intermolecular forces. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance and the intermolecular forces try to draw the particles together.

- gases
  - average kinetic energy of the molecules is larger than average energy of attractions between molecules
  - lack of strong attractive forces allows gases to expand
- liquids
  - denser than gases
  - have a definite volume
  - attractive forces not strong enough to keep molecules from moving allowing liquids to hold shape of container
- solids
  - intermolecular forces hold molecules together and keep them from moving
  - not very compressible
  - crystalline – solids with highly ordered structures

Gas, Liquid and Solid

Gas	assumes both the volume and shape of container is compressible diffusion within a gas occurs rapidly flows readily
Liquid	Assumes the shape of the portion of the container it occupies Does not expand to fill container Is virtually incompressible Diffusion within a liquid occurs slowly Flows readily
Solid	Retains its own shape and volume Is virtually incompressible Diffusion within a solid occurs extremely slowly Does not flow

- state of substance depends on balance between the kinetic energies of the particles and interparticle energies of attraction
- kinetic energies depends on temperature and tend to keep particles apart and moving
- interparticle attractions draw particles together
- condensed phases – liquids and solids because particles are close together compared to gases
- increase temperature forces molecules to be closer together ® increase in strength of intermolecular forces

11.2: Intermolecular Forces

Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold molecules and polyatomic ions together. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as van der Waals forces), and hydrogen bonds.

- intermolecular forces weaker than ionic or covalent bonds
- many properties of liquids reflect strengths of intermolecular forces
- three types of intermolecular forces: dipole-dipole forces, London dispersion forces, and hydrogen-bonding forces
  - also called van der Waals forces
  - less than 15% as strong as covalent or ionic bonds
  - electrostatic in nature, involves attractions between positive and negative species

11.2.1 Ion-Dipole Forces

- Ion-Dipole Force – exists between an ion and partial charge at one end of a polar molecule
- Polar molecules are dipoles
- magnitude of attraction increases as either the charge of ion or magnitude of dipole moment increases

11.2.2 Dipole-Dipole Forces

- dipole-dipole force – exists between neutral polar molecules
- effective only when polar molecules are very close together
- weaker than ion-dipole forces
- for molecules of approximately equal mass and size, the strengths of intermolecular attractions increase with increasing polarity
- increase dipole moment ® increase boiling point

11.2.3 London Dispersion Forces

-
  - interparticle forces that exist between nonpolar atoms or molecules
  - motion of electrons can create an instantaneous dipole moment
  - molecules have to be very close together
  - polarizability – ease in which the charge distribution in a molecule can be distorted
  - greater polarizability ® more easily electron cloud can be distorted to give momentary dipole
  - larger molecules have greater polarizability
  - London dispersion forces increase with increasing molecular size
  - Dispersion forces increase in strength with increasing molecular weight
  - Molecular shape affects intermolecular attractions
  - greater surface contact ® greater boiling point and London dispersion forces
  - dispersion forces operate between all molecules
  - comparing relative strengths of intermolecular attractions:
  - 1) comparable molecular weights and shapes = equal dispersion forces
    - differences in magnitudes of attractive forces due to differences in strengths of dipole-dipole attractions
    - most polar molecule has strongest attractions
  - 2) differing molecular weights = dispersion forces tend to be the decisive ones
    - differences in magnitudes of attractive forces associated with differences in molecular weights
    - most massive molecular has strongest attractions

11.2.4 Hydrogen Bonding

- hydrogen bonding – special type of intermolecular attraction that exists between the hydrogen atom in a polar bond and an unshared electron pair on a nearby electronegative ion or atom
- hydrogen bond with F, N, and O is polar
- density of ice is lower than that of liquid water
- when water freezes the molecules assume the ordered open arrangement ® makes ice less dense than water
- a given mass of ice has a greater volume than the same mass of water
- structure of ice allows the maximum number of hydrogen bonding interactions to exist

11.2.5 Comparing Intermolecular Forces

- dispersion forces found in all substances
- strengths of forces increase with increases molecular weight and also depend on shape
- dipole-dipole forces add to effect of dispersion forces and found in polar molecules
- hydrogen bonds tend to be strongest intermolecular force

11.3: Some Properties of Liquids

Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. Surface tension is the energy required to increase the surface area of a liquid. Surfactants are molecules that reduce the surface tension of polar liquids like water. Capillary action is the phenomenon in which liquids rise up into a narrow tube called a capillary. The viscosity of a liquid is its resistance to flow.

- two properties of liquids: viscosity and surface tension

11.3.1 Viscosity

- viscosity – resistance of a liquid to flow
- the greater the viscosity the more slowly the liquid flows
- measured by timing how long it takes a certain amount of liquid to flow through a thin tube under gravitational forces
- can also be measured by how long it takes steel spheres to fall through the liquid
- viscosity related to ease with which individual molecules of liquid can move with respect to one another
- depends on attractive forces between molecules, and whether structural features exist to cause molecules to be entangled
- viscosity decreases with increasing temperature

11.3.2 Surface Tension

- surface tension – energy required to increase the surface area of a liquid by a unit amount
- surface tension of water at 20° C is 7.29×10^{-2} J/m^2
- 7.29×10^{-2} J/m^2 must be supplied to increase surface area of a given amount of water by 1 m^2
- cohesive forces – intermolecular forces that bind similar molecules
- adhesive forces – intermolecular forces that bind a substance to a surface
- capillary action – rise of liquids up very narrow tubes

11.4: Phase Changes

Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes. Changes of state are examples of phase changes, or phase transitions. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are endothermic. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always exothermic.

11.4.1 Energy Changes Accompanying Phase Changes

-
  - phase changes require energy
  - phase changes to less ordered state requires energy
  - melting process of solid called fusion
  - heat of fusion – enthalpy change of melting a solid
  - ΔH_{fus} water = 6.01 kJ/mol
  - heat of vaporization – heat needed for vaporization of liquid
  - ΔH_{vap} water = 40.67 kJ/mol
  - melting, vaporization, and sublimation are endothermic
  - freezing, condensation, and deposition are exothermic

11.4.2 Heating Curves

-
  - heating curve – graph of temperature of system versus the amount of heat added
  - used to calculate enthalpy changes
  - supercooled water – when water if cooled to a temperature below 0° C

11.4.3 Critical Temperature and Pressure

- ◦ critical temperature – highest temperature at which a substance can exist as a liquid
  ◦ critical pressure – pressure required to bring about liquefaction at critical temperature
  ◦ the greater the intermolecular attractive forces, the more readily gases liquefy ® higher critical temperature
  ◦ cannot liquefy a gas by applying pressure if gas is above critical temperature

11.5: Vapor Pressure

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called vaporization or evaporation, generates a vapor pressure above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via condensation. Eventually, a steady state or dynamic equilibrium is reached.

vapor pressure – measures tendency of a liquid to evaporate

11.5.1 Explaining Vapor Pressure on the Molecular Level

- ◦ dynamic equilibrium – condition when two opposing processes are occurring simultaneously at equal rates
  ◦ vapor pressure of a liquid is the pressure exerted by its vapor when the liquid and vapor states are in dynamic equilibrium

11.5.2 Volatility, Vapor Pressure, and Temperature

- ◦ volatile – liquids that evaporate readily
  ◦ vapor pressure increases with increasing temperature

11.5.3 Vapor Pressure and Boiling Point

- ◦ liquids boil when its vapor pressure equals the external pressure acting on the surface of the liquid
  ◦ temperature of boiling increase with increasing external pressure
  ◦ normal boiling point – boiling point of a liquid at 1 atm
  ◦ higher pressures cause water to boil at higher temperatures

11.6: Phase Diagrams

The states of matter exhibited by a substance under different temperatures and pressures can be summarized graphically in a phase diagram, which is a plot of pressure versus temperature. Phase diagrams contain discrete regions corresponding to the solid, liquid, and gas phases. The solid and liquid regions are separated by the melting curve of the substance, and the liquid and gas regions are separated by its vapor pressure curve, which ends at the critical point.

- phase diagrams – graphical way to summarize conditions under which equilibria exist between the different states of matter
- three important curves:
  ◦ 1) vapor pressure curve of liquid
  ◦ shows equilibrium of liquid and gas phases
  ◦ normal boiling point = point on curve where pressure at 1 atm
  ◦ 2) variation in vapor pressure of solid at it sublimes at different temperatures
  ◦ 3) change in melting point of solid with increasing pressure
  ◦ slopes right as pressure increases
  ◦ higher temperatures needed to melt solids at higher pressures
  ◦ melting point of solid identical to freezing point
    ▪ differ only in temperature direction from which phase change is approached
    ▪ melting point at 1 atm is the normal melting point
- triple point – point at which all three phases are at equilibrium
- gas phase stable at low pressures and high temperatures
- solid phase stable at low temperatures and high pressures

- liquid phase – stable between gas and solids

11.6.1 the Phase diagrams of H_2O and CO_2

- ◦ melting point of CO_2 increases with increasing pressure
  ◦ melting point of H_2O decreases with increasing pressure
  ◦ triple point of H_2O (0.0098° C and 4.58 torr) at lower pressure than CO_2 (-56.4° C and 5.11 atm)
  ◦ solid CO_2 does not melt but sublimes
  ◦ CO_2 does not have a normal melting point but a normal sublimation point
  ◦ CO_2 absorbs energy at ordinary temperatures

11.7: Structure of Solids

A crystalline solid can be represented by its unit cell, which is the smallest identical unit that when stacked together produces the characteristic three-dimensional structure. Solids are characterized by an extended three-dimensional arrangement of atoms, ions, or molecules in which the components are generally locked into their positions. The components can be arranged in a regular repeating three-dimensional array. The smallest repeating unit of a crystal lattice is the unit cell.

- crystalline solid – solid whose atoms, ion, or molecules are ordered in well-defined arrangements
  ◦ flat surfaces or faces that make definite angles
  ◦ regular shapes
- amorphous solid – solid whose particles have no orderly structure
  ◦ lack well-defined faces and shapes
  ◦ mixtures of molecules that do not stack together well
  ◦ large, complicated molecules
  ◦ intermolecular forces vary in strength
  ◦ does not melt at a specific temperature but soften over a temperature range

11.7.1 Unit Cell

- ◦ unit cell – repeating unit of a solid
  ◦ crystal lattice – three-dimensional array of points, each representing an identical environment within the crystal
  ◦ three types of cubic unit cell: primitive cubic, body-centered cubic, and face-centered cubic
  ◦ primitive cubic – lattice points at corners only
  ◦ body-centered cubic – lattice points at corners and center
  ◦ face-centered cubic – lattice points at center of each face and at each corner

11.7.2 The Crystal structure of Sodium Chloride

- ◦ total cation-to-anion ratio of a unit cell must be the same as that for entire crystal

11.7.3 Close Packing of Spheres

- ◦ structures of crystalline solids are those that bring particles in closest contact to maximize the attractive forces
  ◦ most particles that make up solids are spherical
  ◦ two forms of close packing: cubic close packing and hexagonal close packing
  ◦ hexagonal close packing – spheres of the third layer that are placed in line with those of the first layer
  ◦ coordination number – number of particles immediately surrounding a particle in the crystal structure
  ◦ both forms of close packing have coordination number of 12

11.8: Bonding in Solids

The major types of solids are ionic, molecular, covalent, and metallic. Ionic solids consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to

have high melting points and are rather hard. Molecular solids are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. Metallic solids have unusual properties.

Major Types of Solid

Type of Solid	Forms of Unit Particles	Forces Between Particles	Properties	Examples
Molecular	Atoms of molecules	London dispersion, dipole-dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, methane, sucrose, dry ice
Covalent-network	Atoms connected in a network of covalent bonds	Covalent bonds	Very hard, very high melting point, often poor thermal and electrical conduction	Diamond, quartz
Ionic	Positive and negative ions	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts
Metallic	atoms	Metallic bonds	Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile	All metallic elements

11.8.1 Molecular Solids

- molecular solids – atoms or molecules held together by intermolecular forces
- soft, low melting points
- gases or liquids at room temperature from molecular solids at low temperature
- properties depends on strengths of forces and ability of molecules to pack efficiently in three dimensions
- intermolecular forces that depend on close contact are not as effective

11.8.2 Covalent-Network Solids

- covalent-network solids – atoms held together in large networks or chains by covalent bonds
- hard, high melting points

11.8.3 Ionic Solids

- ionic solids – ions held together by ionic bonds
- strength depends on charges of ions
- structure of ionic solids depends on charges and relative sizes of ions

11.8.4 Metallic Solids

- metallic solids – metal atoms
- usually have hexagonal close-packed, cubic close-packed, or body-centered-cubic structures
- each atom has 8 or 12 adjacent atoms
- bonding due to valence electrons that are delocalized throughout entire solid
- strength of bonding increases as number of electrons available for bonding increases
- mobility of electrons make metallic solids good conductors of heat and electricity

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12: SOLIDS AND MODERN MATERIALS

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12.1: Classes of Materials

It can often be quite straightforward to tell materials classes apart by look or feel. Metals are usually more reflective or 'metallic' looking, ceramics are commonly matte and polymers may be shiny or matte, but are typically less dense than either metals or ceramics. Composites may be harder to immediately identify, but the surface may appear non-uniform and/or sectioning the sample may reveal fibres or particles.

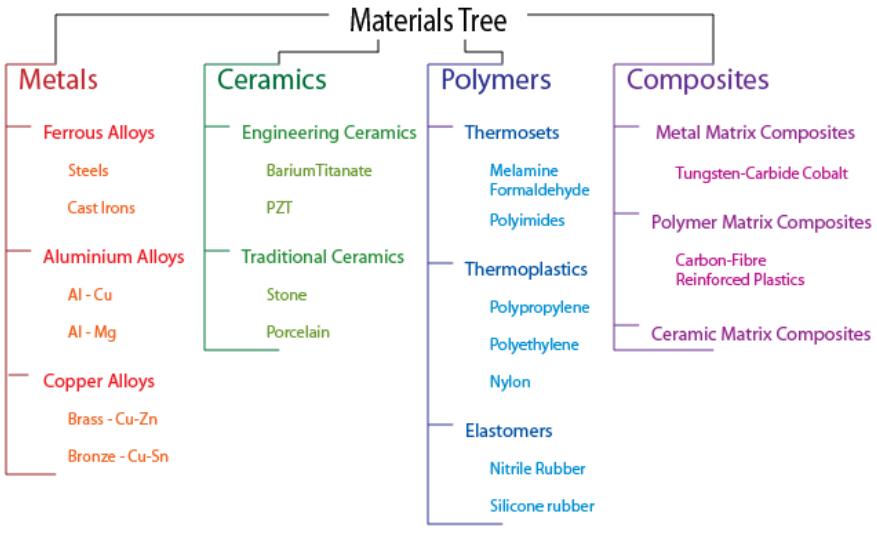
It is useful to note that taking a cross-section can often be helpful in identifying materials used in components as the internal material and/or microstructure may differ from that at the edge.

Some materials may not be quite so easily identified simply from appearance and texture, but considering the factors mentioned can help to narrow down the possibilities. The table below gives a rough guideline to the kinds of properties you would expect from each class, and a few examples:

Properties expected from each class

Class	Common Properties	Examples
Metal	Hard, ductile and conduct heat and electricity	Copper (wires), stainless steel (cutlery)
Polymer	Widely variable, often soft and flexible	Polystyrene (cups), polycarbonate (CDs), polyethylene (plastic bags)
Ceramic	Hard, brittle, resistant to corrosion, electrically non-conductive	Concrete (buildings), PZT (piezoelectric used in lighters and ultrasonic transducers), porcelain (vases, teacups)

The tree-diagram below shows an overview of a variety of materials that might be encountered:



Coatings

Many components may have some kind of coating; a covering of another material designed to improve the surface qualities of the item. The improvement could be for many reasons including: corrosion resistance, appearance, adhesion, wear resistance and scratch resistance.

Different kinds of coating will have different processing methods. It is often possible to deduce the method from the composition (of the coating and the bulk of the component) and the shape of the component.

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Modern Materials

- To become familiar with the properties of some contemporary materials.

In addition to polymers, other materials, such as ceramics, high-strength alloys, and composites, play a major role in almost every aspect of our lives. Until relatively recently, steel was used for any application that required an especially strong and durable material, such as bridges, automobiles, airplanes, golf clubs, and tennis rackets. In the last 15 to 20 years, however, graphite or boron fiber golf clubs and tennis rackets have made wood and steel obsolete for these items. Likewise, a modern jet engine now is largely composed of Ti and Ni by weight rather than steel (Table 12.9.1). The percentage of iron in wings and fuselages is similarly low, which indicates the extent to which other materials have supplanted steel. The Chevrolet Corvette introduced in 1953 was considered unusual because its body was constructed of fiberglass, a composite material, rather than steel; by 1992, Jaguar fabricated an all-aluminum limited-edition vehicle. In fact, the current models of many automobiles have engines that are made mostly of aluminum rather than steel. In this section, we describe some of the chemistry behind three classes of contemporary materials: ceramics, superalloys, and composites.

Table 12.9.1 The Approximate Elemental Composition of a Modern Jet Engine

Element	Percentage by Mass
titanium	38
nickel	37
chromium	12
cobalt	6
aluminum	3
niobium	1
tantalum	0.025

Ceramics

A ceramic is any nonmetallic, inorganic solid that is strong enough for use in structural applications. Traditional ceramics, which are based on metal silicates or aluminosilicates, are the materials used to make pottery, china, bricks, and concrete. Modern ceramics contain a much wider range of components and can be classified as either *ceramic oxides*, which are based on metal oxides such as alumina (Al_2O_3), zirconia (ZrO_2), and beryllia (BeO), or *nonoxide ceramics*, which are based on metal carbides such as silicon carbide (carborundum, SiC) and tungsten carbide (WC), or nitrides like silicon nitride (Si_3N_4) and boron nitride (BN).

All modern ceramics are hard, lightweight, and stable at very high temperatures. Unfortunately, however, they are also rather brittle, tending to crack or break under stresses that would cause metals to bend or dent. Thus a major challenge for materials scientists is to take advantage of the desirable properties of ceramics, such as their thermal and oxidative stability, chemical inertness, and toughness, while finding ways to decrease their brittleness to use them in new applications. Few metals can be used in jet engines, for example, because most lose mechanical strength and react with oxygen at the very high operating temperatures inside the engines (approximately 2000°C). In contrast, ceramic oxides such as Al_2O_3 cannot react with oxygen regardless of the temperature because aluminum is already in its highest possible oxidation state (Al^{3+}). Even nonoxide ceramics such as silicon and boron nitrides and silicon carbide are essentially unreactive in air up to about 1500°C. Producing a high-strength ceramic for service use involves a process called sintering, which fuses the grains into a dense and strong material (Figure 12.9.2).

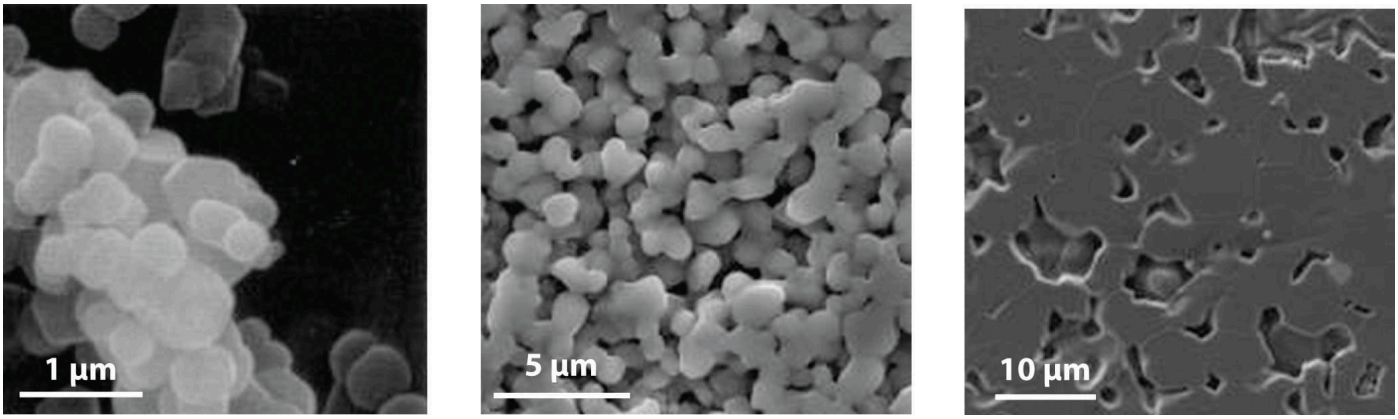


Figure 12.9.2: *Sintering These photos show the effects of sintering magnesium oxide grains: (a) the microstructure before sintering; (b) the microstructure of the ceramic after sintering for two hours at 1250°C; and (c) the microstructure after sintering for two hours at 1450°C. During the sintering process, the grains fuse, forming a dense and strong material.*

Ceramics are hard, lightweight, and able to withstand high temperatures, but they are also brittle.

One of the most widely used raw materials for making ceramics is clay. Clay minerals consist of hydrated alumina (Al_2O_3) and silica (SiO_2) that have a broad range of impurities, including barium, calcium, sodium, potassium, and iron. Although the structures of clay minerals are complicated, they all contain layers of metal atoms linked by oxygen atoms. Water molecules fit between the layers to form a thin film of water. When hydrated, clays can be easily molded, but during high-temperature heat treatment, called *firing*, a dense and strong ceramic is produced.

Because ceramics are so hard, they are easily contaminated by the material used to grind them. In fact, the ceramic often grinds the metal surface of the mill almost as fast as the mill grinds the ceramic! The sol-gel process was developed to address this problem. In this process, a water-soluble precursor species, usually a metal or semimetal alkoxide [$M(OR)_n$] undergoes a hydrolysis reaction to form a cloudy aqueous dispersion called a *sol*. The sol contains particles of the metal or semimetal hydroxide [$M(OH)_n$], which are typically 1–100 nm in diameter. As the reaction proceeds, molecules of water are eliminated from between the $M(OH)_n$ units in a condensation reaction, and the particles fuse together, producing oxide bridges, M–O–M. Eventually, the particles become linked in a three-dimensional network that causes the solution to form a *gel*, similar to a gelatin dessert. Heating the gel to 200°C–500°C causes more water to be eliminated, thus forming small particles of metal oxide that can be amazingly uniform in size. This chemistry starts with highly pure $SiCl_4$ and proceeds via the following reactions starting with the alkoxide formation

$$SiCl_4\,(s) + 4CH_3CH_2OH\,(l) + 4NH_3\,(g) \rightarrow SiO\,(OCH_2CH_3)_4\,(s) + 4NH_4Sl\,(s) \tag{12.1.1}$$

and then the hydrolysis of the alkoxide

$$SiO\,(OCH_2CH_3)_4\,(s) + 4H_2O\,(l) \rightarrow (HO)_3\,Si - OH\,(s) + 4CH_3CH_2OH\,(aq) \tag{12.1.2}$$

ending with the condensation

$$(HO_3)\,Si - OH\,(s) + nHO - Si\,(OH)_3\,(s) \rightarrow (HO_3)\,Si\,(-O - Si\,(OH)_3)_n\,(s) + nH_2O\,(l) \tag{12.1.3}$$

Nature uses the same process to create opal gemstones.

Superalloys

Superalloys are high-strength alloys, often with a complex composition, that are used in systems requiring mechanical strength, high surface stability (minimal flaking or pitting), and resistance to high temperatures. The aerospace industry, for example, requires materials that have high strength-to-weight ratios to improve the fuel efficiency of advanced propulsion systems, and these systems must operate safely at temperatures greater than 1000°C.

Superalloys are used in systems requiring mechanical strength, minimal flaking or pitting, and high-temperature resistance.

Although most superalloys are based on nickel, cobalt, or iron, other metals are used as well. Pure nickel or cobalt is relatively easily oxidized, but adding small amounts of other metals (Al, Co, Cr, Mo, Nb, Ti, and W) results in an alloy that has superior properties. Consequently, most of the internal parts of modern gas turbine jet engines are now made of superalloys based on either nickel (used in blades and disks) or cobalt (used in vanes, combustion chamber liners, and afterburners). The cobalt-based superalloys are not as strong as the nickel-based ones, but they have excellent corrosion resistance at high temperatures.

Other alloys, such as aluminum–lithium and alloys based on titanium, also have applications in the aerospace industry. Because aluminum–lithium alloys are lighter, stiffer, and more resistant to fatigue at high temperatures than aluminum itself, they are used in engine parts and in the metal "skins" that cover wings and bodies. Titanium's high strength, corrosion resistance, and lightweight properties are equally desirable for applications where minimizing weight is important (as in airplanes). Unfortunately, however, metallic titanium reacts rapidly with air at high temperatures to form TiN and TiO_2. The welding of titanium or any similar processes must therefore be carried out in an argon or inert gas atmosphere, which adds significantly to the cost. Initially, titanium and its alloys were primarily used in military applications, but more recently, they have been used as components of the airframes of commercial planes, in ship structures, and in biological implants.

Composite Materials

Composite materials have at least two distinct components: the matrix (which constitutes the bulk of the material) and fibers or granules that are embedded within the matrix and limit the growth of cracks by pinning defects in the bulk material (Figure 12.9.3). The resulting material is stronger, tougher, stiffer, and more resistant to corrosion than either component alone. Composites are thus the nanometer-scale equivalent of reinforced concrete, in which steel rods greatly increase the mechanical strength of the cement matrix, and are extensively used in the aircraft industry, among others. For example, the Boeing 777 is 9% composites by weight, whereas the newly developed Boeing 787 is 50% composites by weight. Not only does the use of composite materials reduce the weight of the aircraft, and therefore its fuel consumption, but it also allows new design concepts because composites can be molded. Moreover, by using composites in the Boeing 787 multiple functions can be integrated into a single system, such as acoustic damping, thermal regulation, and the electrical system.

Three distinct types of composite material are generally recognized, distinguished by the nature of the matrix. These are polymer-matrix composites, metal-matrix composites, and ceramic-matrix composites.

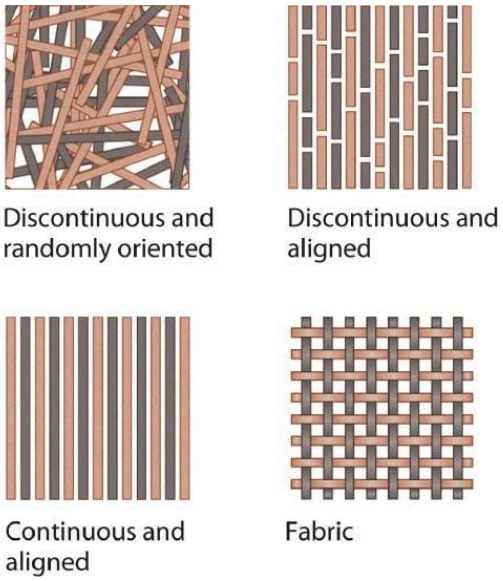


Figure 12.9.3: *Some Possible Arrangements of Fibers in Fiber-Reinforced Composite Materials The arrangements shown range from discontinuous and randomly oriented to continuous and aligned. The fibers limit the growth of cracks by pinning defects within the matrix.*

Composites are stronger, tougher, stiffer, and more resistant to corrosion than their components alone.

Fiberglass is a polymer-matrix composite that consists of glass fibers embedded in a polymer, forming tapes that are then arranged in layers impregnated with epoxy. The result is a strong, stiff, lightweight material that is resistant to chemical degradation. It is not strong enough, however, to resist cracking or puncturing on impact. Stronger, stiffer polymer-matrix composites contain fibers of carbon (graphite), boron, or polyamides such as Kevlar. High-tech tennis rackets and golf clubs as well as the skins of modern military aircraft such as the “stealth” F-117A fighters and B-2 bombers are made from both carbon fiber–epoxy and boron fiber–epoxy composites. Compared with metals, these materials are 25%–50% lighter and thus reduce operating costs. Similarly, the space shuttle payload bay doors and panels are made of a carbon fiber–epoxy composite. The structure of the Boeing 787 has been described as essentially one giant macromolecule, where everything is fastened through cross-linked chemical bonds reinforced with carbon fiber.

Metal-matrix composites consist of metals or metal alloys reinforced with fibers. They offer significant advantages for high-temperature applications but pose major manufacturing challenges. For example, obtaining a uniform distribution and alignment of the reinforcing fibers can be difficult, and because organic polymers cannot survive the high temperatures of molten metals, only fibers composed of boron, carbon, or ceramic (such as silicon carbide) can be used. Aluminum alloys reinforced with boron fibers are used in the aerospace industry, where their strength and lightweight properties make up for their relatively high cost. The skins of hypersonic aircraft and structural units in the space shuttle are made of metal-matrix composites.

Ceramic-matrix composites contain ceramic fibers in a ceramic matrix material. A typical example is alumina reinforced with silicon carbide fibers. Combining the two very high-melting-point materials results in a composite that has excellent thermal stability, great strength, and corrosion resistance, while the SiC fibers reduce brittleness and cracking. Consequently, these materials are used in very high-temperature applications, such as the leading edge of wings of hypersonic airplanes and jet engine parts. They are also used in the protective ceramic tiles on the space shuttle, which contain short fibers of pure SiO_2 mixed with fibers of an aluminum–boron–silicate ceramic. These tiles are excellent thermal insulators and extremely light (their density is only about 0.2 g/cm^3). Although their surface reaches a temperature of about 1250°C during reentry into Earth’s atmosphere, the temperature of the underlying aluminum alloy skin stays below 200°C.

Example 12.1.1:

An engineer is tasked with designing a jet ski hull. What material is most suited to this application? Why?

Given: design objective

Asked for: most suitable material

Strategy:

Determine under what conditions the design will be used. Then decide what type of material is most appropriate.

Solution:

A jet ski hull must be lightweight to maximize speed and fuel efficiency. Because of its use in a marine environment, it must also be resistant to impact and corrosion. A ceramic material provides rigidity but is brittle and therefore tends to break or crack under stress, such as when it impacts waves at high speeds. Superalloys provide strength and stability, but a superalloy is probably too heavy for this application. Depending on the selection of metals, it might not be resistant to corrosion in a marine environment either. Composite materials, however, provide strength, stiffness, and corrosion resistance; they are also lightweight materials. This is not a high-temperature application, so we do not need a metal-matrix composite or a ceramic-matrix composite. The best choice of material is a polymer-matrix composite with Kevlar fibers to increase the strength of the composite on impact.

Exercise 12.1.1

In designing a new generation of space shuttle, National Aeronautics and Space Administration (NASA) engineers are considering thermal-protection devices to protect the skin of the craft. Among the materials being considered are titanium- or nickel-based alloys and silicon-carbide ceramic reinforced with carbon fibers. Why are these materials suitable for this application?

Answer: Ti- or Ni-based alloys have a high strength-to-weight ratio, resist corrosion, and are safe at high temperatures. Reinforced ceramic is lightweight; has high thermal and oxidative stability; and is chemically inert, tough, and impact resistant.

Summary

Ceramics are nonmetallic, inorganic solids that are typically strong; they have high melting points but are brittle. The two major classes of modern ceramics are ceramic oxides and nonoxide ceramics, which are composed of nonmetal carbides or nitrides. The production of ceramics generally involves pressing a powder of the material into the desired shape and sintering at a temperature just below its melting point. The necessary fine powders of ceramic oxides with uniformly sized particles can be produced by the **sol-gel process**. **Superalloys** are new metal phases based on cobalt, nickel, or iron that exhibit unusually high temperature stability and resistance to oxidation. **Composite materials** consist of at least two phases: a matrix that constitutes the bulk of the material and fibers or granules that act as a reinforcement. **Polymer-matrix composites** have reinforcing fibers embedded in a polymer matrix. **Metal-matrix composites** have a metal matrix and fibers of boron, graphite, or ceramic. **Ceramic-matrix composites** use reinforcing fibers, usually also ceramic, to make the matrix phase less brittle.

Key Takeaway

- Materials that have contemporary applications include ceramics, high-strength alloys, and composites, whose properties can be modified as needed.

Conceptual Problems

1. Can a compound based on titanium oxide qualify as a ceramic material? Explain your answer.
2. What features make ceramic materials attractive for use under extreme conditions? What are some potential drawbacks of ceramics?
3. How do composite materials differ from the other classes of materials discussed in this chapter? What advantages do composites have versus other materials?
4. How does the matrix control the properties of a composite material? What is the role of an additive in determining the properties of a composite material?

Contributors

- Anonymous

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12.2: MATERIALS FOR STRUCTURE

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12.2.1: Concrete

12.2.2: Steel

12.2.3: Aluminum

12.2.4: Polymers

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12.2.1: Concrete

The most popular building material in the world today, concrete was first developed and exploited by the ancient Romans, who used it to create monumental public spaces such as **aqueducts**, churches, baths, and the Colosseum. Although concrete is a durable material with many building applications, the design of Roman concrete structures reinforced Roman ideas about social status and imperial power. This chapter explores the rich history of concrete and its legacy in the modern world, touching upon the role of concrete in ancient Rome, today's technical advances in concrete construction, and concrete's environmental drawbacks. The chapter also examines how concrete construction is shaped by societal ideals today, just as it was by societal ideas in ancient Rome.

Pourable, moldable, durable, waterproof, and relatively easy and inexpensive to manufacture, concrete is the world's most popular building material. We live, work, and play on and in buildings and roads constructed from it. Architects exploit its properties to create artistic tours de force as well as utilitarian monuments

Origin of Concrete

As far back as the sixth millennium (6000–5000 BCE), the ancient Mesopotamians knew that heating calcium carbonate, a substance occurring naturally in limestone rocks, creates a new substance, known today as quicklime, in a process described chemically as $CACO_3$ + heat(1000° C) =CO_2 + CaO. This chemical reaction releases carbon dioxide into the atmosphere (more on this later). The resulting material, when mixed with water, bonds to other surfaces. The early residents of Çatalhöyük, an ancient city in modern-day Turkey used this substance to coat their walls, providing a surface for painted decoration.

Modern Concrete

Despite more highly mechanized manufacturing techniques, the process of creating concrete still relies on the basic chemical reaction exploited by the Romans, the reaction that releases carbon dioxide, a major pollutant, into the atmosphere. The world's yearly production of concrete has been rising steadily and today is over four billion tons. Concrete production is responsible for nearly eight percent of the anthropogenic (human-made) greenhouse gases released into the air. By some estimates, the external climate and health damages caused by concrete production amount to approximately 74 percent of the value of the industry itself, putting the external costs of concrete higher than natural gas and oil and only slightly less than coal. As even more concrete is produced, the amount of carbon dioxide will also rise unless we develop smarter, greener methods of production. Concrete manufacturers recognize this problem, but any solution will have to be cost effective for worldwide adoption to take place.

The first step in making concrete is to produce cement as discussed in the video below.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

An additional cost of manufacturing concrete is the need for sand as a component of the finished product. Today, sand is becoming an increasingly rare and sought-after commodity. As the Romans knew, only sand worn by water (river or ocean sand), not sand that has been exposed to the elements (desert sand), is suitable. While there are problems are connected with new construction, older concrete structures pose other issues. Most modern concrete is reinforced by metal bars that lead to eventual cracking as the metal expands and contracts. Can we recycle ruined concrete buildings? How can we stabilize and repair buildings? Engineers are working to develop new technologies that can sense imminent structural issues before a bridge or building collapses. To prevent damage in new construction, engineers developed Smartcrete, a form of concrete that can repair itself. New methods of concrete construction such as Ductal, which requires no metal, and the use of cloth as a framing material

are also potential answers to this problem.

Although some striking modern architectural monuments have been built from concrete—the Guggenheim Museum in New York, for example—many consider modern concrete stark and ugly because of the many utilitarian buildings constructed from it. Because, unlike the Romans, we can make concrete with a smooth surface, it is not necessary for us to cover it with other materials.

New concrete technologies continue to emerge. Among the possibilities is concrete laid by robots. Acknowledging the close link between buildings and social structure allows us to wonder if there might be hidden costs to this technology. What types of workforce changes would occur if machines took over this aspect of building construction? Would using robots free humans to do other things or would it merely eliminate a large category of jobs?

Future of Concrete

Building construction remains the primary use of concrete today. Might there not be other uses for such a versatile material beyond architecture? Architects, engineers, and others are beginning to address this question. For example, kitchen designers are using concrete for countertops, taking advantage of its durability, cost effectiveness, modern appearance, and ability to resist water. People are even considering how ancient Roman concrete might be used to address sea level rise associated with global warming.

To encourage thinking about a common material in a different light, the American Society for Civil Engineering sponsors an annual concrete canoe contest. This challenge forces students to broaden their ideas about possible applications for this common material. Engineering students from across the US attempt to build and race a concrete canoe. They are judged not only on the results of the race, but also on their design concept. Concrete is certainly not the first material that comes to mind when thinking about canoes, although it is waterproof. But a concrete canoe suggests that if we think beyond the limits imposed on the use of concrete by our societal worldview and historical traditions, we may be able to find newer and more effective ways to use this versatile material.

Contributed By

Excerpted from a longer piece by Mary Ann Eaverly, University of Florida

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12.2.2: Steel

23.3: Metallurgy of Iron and Steel

Learning Objectives

- Outline the general approach for the metallurgy of iron into steel

The early application of iron to the manufacture of tools and weapons was possible because of the wide distribution of iron ores and the ease with which iron compounds in the ores could be reduced by carbon. For a long time, charcoal was the form of carbon used in the reduction process. The production and use of iron became much more widespread about 1620, when coke was introduced as the reducing agent. Coke is a form of carbon formed by heating coal in the absence of air to remove impurities.

The overall reaction for the production of iron in a blast furnace is as follows:

$$\mathrm{Fe_2O_3(s) + 3C(s) \xrightarrow{\Delta} 2Fe(l) + 3CO(g)} \tag{12.2.2.1}$$

The actual reductant is CO, which reduces Fe_2O_3 to give Fe(l) and CO_2(g) (Equation 12.2.2.1); the CO_2 is then reduced back to CO by reaction with excess carbon. As the ore, lime, and coke drop into the furnace (Figure 12.2.2.1), any silicate minerals in the ore react with the lime to produce a low-melting mixture of calcium silicates called slag, which floats on top of the molten iron. Molten iron is then allowed to run out the bottom of the furnace, leaving the slag behind. Originally, the iron was collected in pools called pigs, which is the origin of the name pig iron.

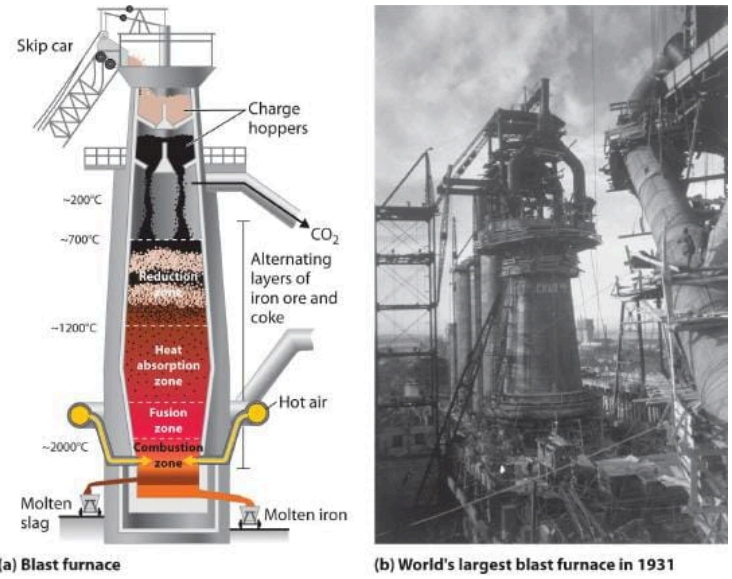


Figure 12.2.2.1: *A Blast Furnace for Converting Iron Oxides to Iron Metal. (a) The furnace is charged with alternating layers of iron ore (largely Fe_2O_3) and a mixture of coke (C) and limestone ($CaCO_3$). Blasting hot air into the mixture from the bottom causes it to ignite, producing CO and raising the temperature of the lower part of the blast furnace to about 2000°C. As the CO that is formed initially rises, it reduces Fe_2O_3 to form CO_2 and elemental iron, which absorbs heat and melts as it falls into the hottest part of the furnace. Decomposition of $CaCO_3$ at high temperatures produces CaO (lime) and additional CO_2, which reacts with excess coke to form more CO. (b) This blast furnace in Magnitogorsk, Russia, was the largest in the world when it was built in 1931.*

The first step in the metallurgy of iron is usually roasting the ore (heating the ore in air) to remove water, decomposing carbonates into oxides, and converting sulfides into oxides. The oxides are then reduced in a blast furnace that is 80–100 feet high and about 25 feet in diameter (Figure 12.2.2.2) in which the roasted ore, coke, and limestone (impure $CaCO_3$) are introduced continuously into the top. Molten iron and slag are withdrawn at the bottom. The entire stock in a furnace may weigh several hundred tons.

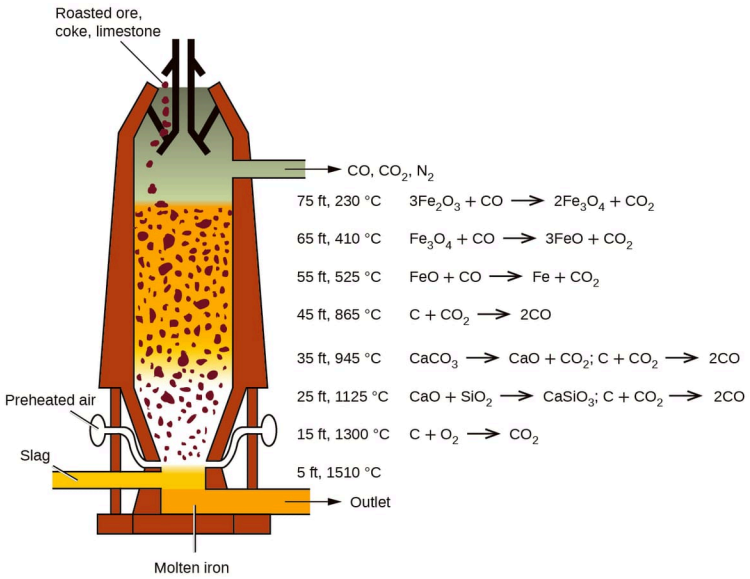


Figure 12.2.2.2:Within a blast furnace, different reactions occur in different temperature zones. Carbon monoxide is generated in the hotter bottom regions and rises upward to reduce the iron oxides to pure iron through a series of reactions that take place in the upper regions.

A diagram of a blast furnace is shown. The furnace has a cylindrical shape that is oriented vertically. A pipe at the lower left side of the figure is shaded yellow and is labeled “Slag.” It connects to an interior chamber. Situated at a level just below this piping on the right side of the figure is another pipe that is shaded orange. It opens at the lower right side of the figure. The orange-shaded substance at the bottom of the chamber that matches the contents of the pipe to its right is labeled “Molten iron.” The pipe has an arrow exiting to the right pointing to the label “Outlet.” Just above the slag and molten iron regions is narrower tubing on both the left and right sides of the chamber which lead slightly up and out from the central chamber to small oval shapes. These shapes are labeled, “Preheated air.” The region just above the points of entry of these two pipes or tubes into the chamber is a white region in which small rust-colored chunks of material appear suspended. This region tapers slightly to the bottom of the furnace. The region above has an orange background in which small rust-colored chunks are similarly suspended. This region fills nearly half of the interior of the furnace. Above this region is a grey shaded region. At the very top of the furnace, black line segments indicate directed openings through which small rust-colored chunks of material appear to be entering the furnace from the top. This material is labeled, “Roasted ore, coke, limestone.” Exiting the grey shaded interior region to the right is a pipe. An arrow points right exiting the pipe pointing to the label “C O, C O subscript 2, N subscript 2.” At the right side of the figure, furnace heights are labeled in order of increasing height between the outlet pipes, followed by temperatures and associated chemical reactions. Just above the pipe labeled, “Outlet,” no chemical equation appears right of, “5 f t, 1510 degrees C.” To the right of, “15 f t, 1300 degrees C,” is the equation, “C plus O subscript 2 right pointing arrow C O subscript 2.” To the right of, “25 f t, 1125 degrees C,” are the two equations, “C a O plus S i O subscript 2 right pointing arrow C a S i O subscript 3” and “C plus C O subscript 2 right pointing arrow 2 C O.” To the right of, “35 f t, 945 degrees C,” are the two equations, “C a C O subscript 3 right pointing arrow C a O plus C O subscript 2,” and, “C plus C O subscript 2 right pointing arrow 2 C O.” To the right of, “45 f t, 865 degrees C,” is the equation, “C plus C O subscript 2 right pointing arrow 2 C O.” To the right of, “55 f t, 525 degrees C,” is the equation “F e O plus C O right pointing arrow F e plus C O subscript 2.” To the right of, “65 f t, 410 degrees C,” is the equation, “F e subscript 3 O subscript 4 plus C O right pointing arrow 3 F e O plus C O subscript 2.” To the right of “75 f t, 230 degrees C,” is the equation, “3 F e subscript 2 O subscript 3 plus C O right pointing arrow 2 F e subscript 3 O subscript 4 plus C O subscript 2.”

Near the bottom of a furnace are nozzles through which preheated air is blown into the furnace. As soon as the air enters, the coke in the region of the nozzles is oxidized to carbon dioxide with the liberation of a great deal of heat. The hot carbon dioxide passes upward through the overlying layer of white-hot coke, where it is reduced to carbon monoxide:

$$\mathrm{CO_2}(g) + \mathrm{C}(s) \longrightarrow 2\,\mathrm{CO}(g)$$

The carbon monoxide serves as the reducing agent in the upper regions of the furnace. The individual reactions are indicated in Figure 12.2.2.2. The iron oxides are reduced in the upper region of the furnace. In the middle region, limestone (calcium carbonate) decomposes, and the resulting calcium oxide combines with silica and silicates in the ore to form slag. The slag is mostly calcium silicate and contains most of the commercially unimportant components of the ore:

$$\mathrm{CaO}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{CaSiO_3}(l)$$

Just below the middle of the furnace, the temperature is high enough to melt both the iron and the slag. They collect in layers at the bottom of the furnace; the less dense slag floats on the iron and protects it from oxidation. Several times a day, the slag and molten iron are withdrawn from the furnace. The iron is transferred to casting machines or to a steelmaking plant (Figure 12.2.2.3).

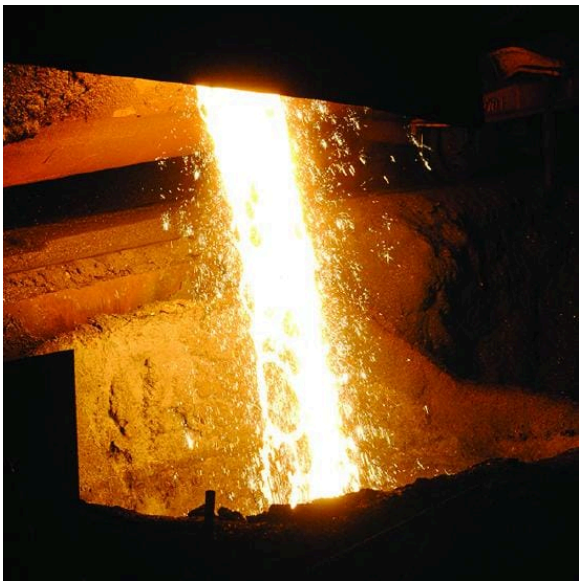


Figure 12.2.2.3:Molten iron is shown being cast as steel. (credit: Clint Budd)

This figure shows a photo of molten iron. A bright yellow-orange glow appears just left of center in the figure. Smoke appears to be rising toward the top center of the figure. Just below and to the right, sparks appear to be falling.

Steel

Much of the iron produced is refined and converted into steel. Steel is made from iron by removing impurities and adding substances such as manganese, chromium, nickel, tungsten, molybdenum, and vanadium to produce alloys with properties that make the material suitable for specific uses. Most steels also contain small but definite percentages of carbon (0.04%–2.5%). However, a large part of the carbon contained in iron must be removed in the manufacture of steel; otherwise, the excess carbon would make the iron brittle. However, there is not just one substance called steel - they are a family of alloys of iron with carbon or various metals.

Impurities in the iron from the Blast Furnace include carbon, sulfur, phosphorus and silicon, which have to be removed.

- **Removal of sulfur**: Sulfur has to be removed first in a separate process. Magnesium powder is blown through the molten iron and the sulfur reacts with it to form magnesium sulfide. This forms a slag on top of the iron and can be removed.

$$Mg + S \rightarrow MgS \tag{12.2.2.2}$$

- **Removal of carbon:** The still impure molten iron is mixed with scrap iron (from recycling) and oxygen is blown on to the mixture. The oxygen reacts with the remaining impurities to form various oxides. The carbon forms carbon monoxide. Since this is a gas it removes itself from the iron! This carbon monoxide can be cleaned and used as a fuel gas.
- **Removal of other elements:** Elements like phosphorus and silicon react with the oxygen to form acidic oxides. These are removed using quicklime (calcium oxide) which is added to the furnace during the oxygen blow. They react to form compounds such as calcium silicate or calcium phosphate which form a slag on top of the iron.

Table 12.2.2.1*: Special Steels*

	iron mixed with	special properties	uses include
stainless steel	chromium and nickel	resists corrosion	cutlery, cooking utensils, kitchen sinks, industrial equipment for food and drink processing
titanium steel	titanium	withstands high temperatures	gas turbines, spacecraft
manganese steel	manganese	very hard	rock-breaking machinery, some railway track (e.g. points), military helmets

Cast iron has already been mentioned above. This section deals with the types of iron and steel which are produced as a result of the steel-making process.

- **Wrought iron**: If all the carbon is removed from the iron to give high purity iron, it is known as wrought iron. Wrought iron is quite soft and easily worked and has little structural strength. It was once used to make decorative gates and railings, but these days mild steel is normally used instead.
- **Mild steel**: Mild steel is iron containing up to about 0.25% of carbon. The presence of the carbon makes the steel stronger and harder than pure iron. The higher the percentage of carbon, the harder the steel becomes. Mild steel is used for lots of things - nails, wire, car bodies, ship building, girders and bridges amongst others.
- **High carbon steel**: High carbon steel contains up to about 1.5% of carbon. The presence of the extra carbon makes it very hard, but it also makes it more brittle. High carbon steel is used for cutting tools and masonry nails (nails designed to be driven into concrete blocks or brickwork without bending). High carbon steel tends to fracture rather than bend if mistreated.
- **Special steels**: These are iron alloyed with other metals (Table 12.2.2.1).

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video: You can watch an animation of steelmaking that walks you through the process (Steelmaking animation, YouTube [www.youtube.com]).

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- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

- Jim Clark (Chemguide.co.uk)

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12.2.3: Aluminum

Aluminum is easily oxidized, and so its ore, Al_2O_3, is difficult to reduce. In fact water is reduced rather than $Al^{3+}(aq)$, and so electrolysis must be carried out in a molten salt. Even this is difficult because the melting point of Al_2O_3 is above 2000°C—a temperature which is very difficult to maintain.

The first successful method for reducing Al_2O_3 is the one still used today. It was developed in the United States in 1886 by Charles Hall (1863 to 1914), who was then 23 years old and fresh out of Oberlin College. Hall realized that if Al_2O_3 were dissolved in another molten salt, the melting point of the mixture would be lower than for either pure substance. The substance Hall used was cryolite, Na_3AlF_6, in which the Al_2O_3 can be dissolved at just over 1000°C.

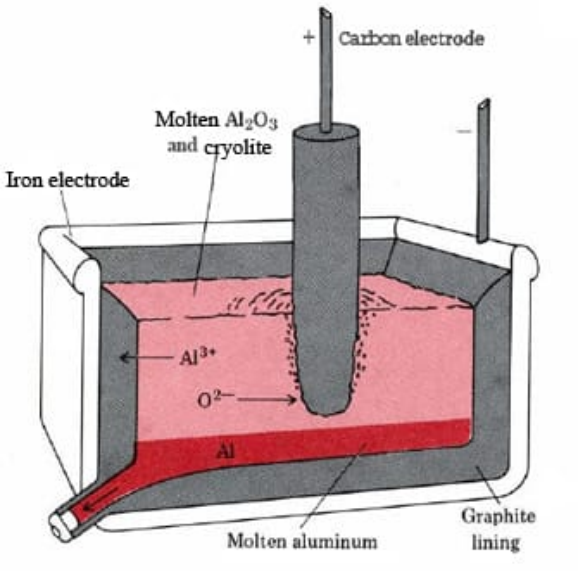


Figure 12.2.3.1: The Hall process.

The electrolytic cell used for the Hall process. (Figure 12.2.3.1) consists of a steel box lined with graphite. This contains the molten Na_3AlF_6 and Al_2O_3 and also serves as the cathode. The anode is a large cylinder of carbon. Passage of electrical current maintains the high temperature of the cell and causes the following half-equations to occur:

$$Al^{3+} + 3e^- \rightarrow Al(l) \tag{12.2.3.1}$$

$$2O^{2-} + C(s) \rightarrow CO_2(g) + 4e^- \tag{12.2.3.2}$$

Since the carbon anode is consumed by the oxidation half-equation, it must be replaced periodically. The video below shows the process

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Aluminum production requires vast quantities of electrical energy, both to maintain the high temperature and to cause half-equations 12.2.3.1 and 12.2.3.2 to occur. Currently about 5 percent of the total electrical energy produced in the United States goes

into the Hall process. Much of this energy comes from combustion of fossil fuels and hence consumes a valuable, nonrenewable resource. Since Al is protected from oxidation back to Al_2O_3 by a surface coating of oxide, it is a prime candidate for recycling, as well as for applications such as house siding, where it is expected to remain for a long time. Throwing away aluminum beverage cans, on the other hand, is a tremendous waste of energy.

Several other easily oxidized metals are currently produced by electrolysis, but not in such large quantities as Al. Mg is obtained by electrolyzing molten $MgCl_2$ which is derived from seawater, and Na and Ca are produced together from a molten mixture of NaCl and $CaCl_2$.

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12.2.4: Polymers

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the bold terms in the context of this topic.

- Aside from their high molar masses, how do synthetic polymers differ from ordinary molecular solids?
- Polymers can be classified according to their chemical composition, their physical properties, and their general application. For each of these three categories, name two examples that that might be considered when adapting a polymer to a particular end-use.
- and a ***thermoset***, and comment on the molecular basis for their different properties, including crystallinity.
- Describe the two general methods of polymer synthesis.
- Name two kinds each of commercially-important synthetic thermoplastics and thermosets, and specify some of their principal uses.
- Name two kinds of commercially-important natural polymers.
- Describe some of the concerns and sources of small-molecule release from polymers.
- What are some of the problems connected with recycling or re-use of polymeric materials?

Plastics and natural materials such as rubber or cellulose are composed of very large molecules called polymers. Polymers are constructed from relatively small molecular fragments known as monomers that are joined together. Wool, cotton, silk, wood and leather are examples of natural polymers that have been known and used since ancient times. This group includes biopolymers such as proteins and carbohydrates that are constituents of all living organisms.

Synthetic polymers, which includes the large group known as plastics, came into prominence in the early twentieth century. Chemists' ability to engineer them to yield a desired set of properties (strength, stiffness, density, heat resistance, electrical conductivity) has greatly expanded the many roles they play in the modern industrial economy. This Module deals mostly with synthetic polymers, but will include a synopsis of some of the more important natural polymers. It will close with a summary of some of the very significant environmental problems created by the wide use of plastics.

Polymers and "pure substances"

Let's begin by looking at an artificial polymer that is known to everyone in the form of flexible, transparent **plastic bags**: *polyethylene*. It is also the simplest polymer, consisting of random-length (but generally very long) chains made up of two-carbon units.

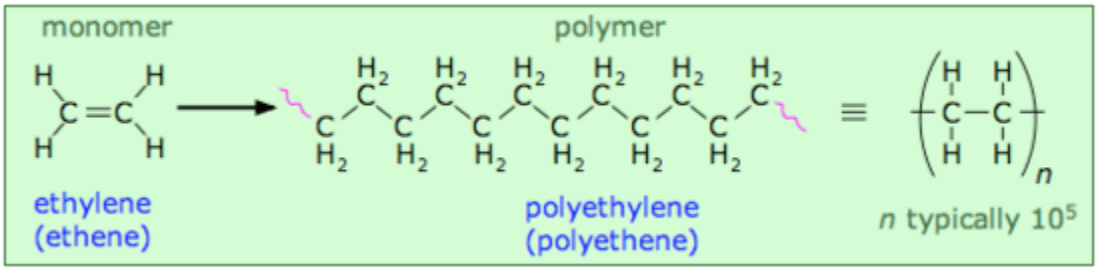


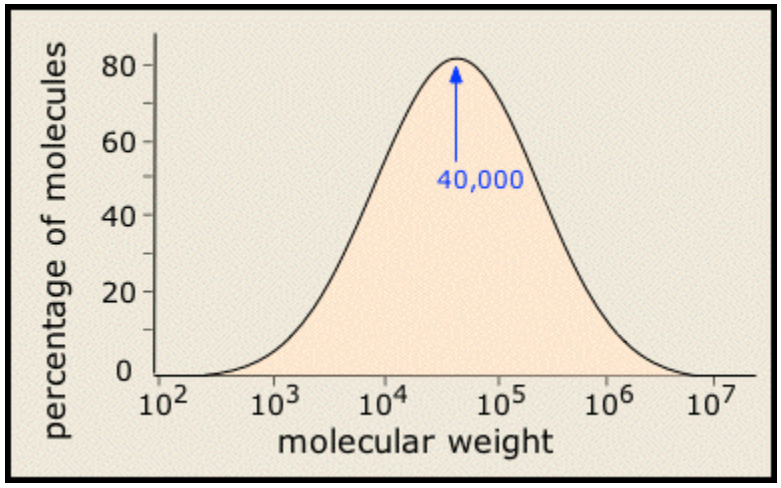
Figure 12.2.4.1: Polymers

Ethylene is shown as a monomer. A long chain containing multiple repeating ethylene is known as polyethylene which is a polymer.

You will notice some "fuzziness" in the way that the polyethylene structures are represented above. The squiggly lines at the ends of the long structure indicate that the same pattern extends indefinitely. The more compact notation on the right shows the minimal repeating unit enclosed in brackets overprinted with a dash; this means the same thing and is the preferred way of depicting polymer structures.

In most areas of chemistry, a "pure substance" has a definite structure, molar mass, and properties. It turns out, however, that few

polymeric substances are uniform in this way. This is especially the case with synthetic polymers, whose molecular weights cover a range of values, as may the sequence, orientation, and connectivity of the individual monomers. So most synthetic polymers are really *mixtures* rather than pure substances in the ordinary chemical sense of the term. Their molecular weights are typically distributed over a wide range.



Percentage of molecules is normally distributed over a wide range of molecular weight. The peak is located at approximately 40,000 for 80 percent of molecules.

Figure 12.2.4.1: Polymers

Don't be misled by chemical formulas that depict polymers such as polyethylene as reasonably straight chains of substituted carbon atoms. Free rotation around C—C bonds allows long polymer molecules to curl up and and tangle very much like spaghetti (Figure 12.2.4.2). Thus polymers generally form *amorphous* solids. There are, however, ways in which certain polymers can be partially oriented.



Figure 12.2.4.2: The structure of polymers more closely resemble spaghetti than the linear structure in Figure 12.2.4.1. from Wikipedia

Classification of polymers

Polymers can be classified in ways that reflect their chemical makeup, or perhaps more importantly, their properties and applications. Many of these factors are strongly interdependent, and most are discussed in much more detail in subsequent sections of this page.

Chemistry

- Nature of the monomeric units
- Average chain length and molecular weight
- *Homopolymers* (one kind of monomeric unit) or *copolymers*;
- Chain topology: how the monomeric units are connected
- Presence or absence of cross-branching
- Method of polymerization

Properties

- Density
- Thermal properties — can they soften or melt when heated?
- Degree of crystallinity
- Physical properties such as hardness, strength, machineability.
- Solubility, permeability to gases

Applications

- molded and formed objects ("plastics")
- sheets and films
- elastomers (i.e., elastic polymers such as rubber)
- adhesives
- coatings, paints, inks
- fibers and yarns

Physical properties of polymers

The physical properties of a polymer such as its strength and flexibility depend on:

- *chain length* - in general, the longer the chains the stronger the polymer;
- *side groups* - polar side groups (including those that lead to hydrogen bonding) give stronger attraction between polymer chains, making the polymer stronger;
- *branching* - straight, unbranched chains can pack together more closely than highly branched chains, giving polymers that have higher density, are more crystalline and therefore stronger;
- *cross-linking* - if polymer chains are linked together extensively by covalent bonds, the polymer is harder and more difficult to melt.

Amorphous and crystalline polymers

The spaghetti-like entanglements of polymer molecules tend to produce amorphous solids, but it often happens that some parts can become sufficiently aligned to produce a region exhibiting crystal-like order, so it is not uncommon for some polymeric solids to consist of a random mixture of amorphous and crystalline regions. As might be expected, shorter and less-branched polymer chains can more easily organize themselves into ordered layers than have can long chains. Hydrogen-bonding between adjacent chains also helps, and is very important in fiber-forming polymers both synthetic (Nylon 6.6) and natural (cotton cellulose).

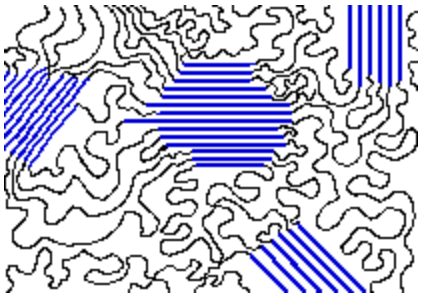


Figure 12.2.4.3: The crystalline parts of this polymer are shown in blue.

Pure crystalline solids have definite melting points, but polymers, if they melt at all, exhibit a more complex behavior. At low temperatures, the tangled polymer chains tend to behave as rigid glasses. For example, the natural polymer that we call *rubber* becomes hard and brittle when cooled to liquid nitrogen temperature. Many synthetic polymers remain in this state to well above room temperature.

The melting of a crystalline compound corresponds to a sudden loss of long-range order; this is the fundamental reason that such solids exhibit definite melting points, and it is why there is no intermediate form between the liquid and the solid states. In amorphous solids there is no long-range order, so there is no melting point in the usual sense. Such solids simply become less and less viscous as the temperature is raised.

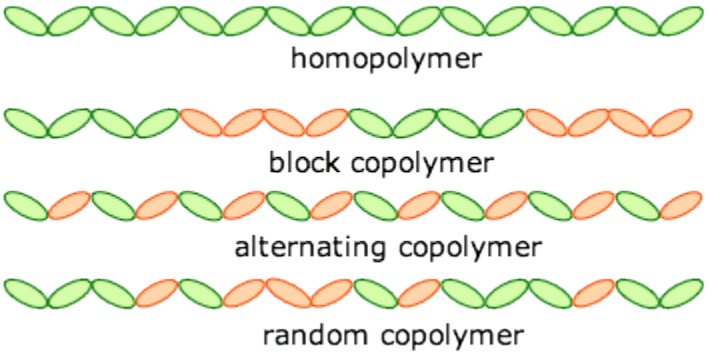
In some polymers (known as *thermoplastics*) there is a fairly definite softening point that is observed when the thermal kinetic energy becomes high enough to allow internal rotation to occur within the bonds and to allow the individual molecules to slide independently of their neighbors, thus rendering them more flexible and deformable. This defines the *glass transition temperature* t_g .

Depending on the degree of crystallinity, there will be a higher temperature, the *melting point* t_m , at which the crystalline regions come apart and the material becomes a viscous liquid. Such liquids can easily be injected into molds to manufacture objects of various shapes, or extruded into sheets or fibers. Other polymers (generally those that are highly cross-linked) do not melt at all; these are known as *thermosets*. If they are to be made into molded objects, the polymerization reaction must take place within the molds — a far more complicated process. About 20% of the commercially-produced polymers are thermosets; the remainder are thermoplastics.

2 Thermoplastic polymer structures

Homopolymers and heteropolymers

Copolymerization is an invaluable tool for "tuning" polymers so that they have the right combination of properties for an application. For example, homopolymeric polystyrene is a rigid and very brittle transparent thermoplastic with a glass transition temperature of 97°C. Copolymerizing it with acrylonitrile yields an alternating "SAN" copolymer in which t_g is raised to 107°, making it useable for transparent drink containers.

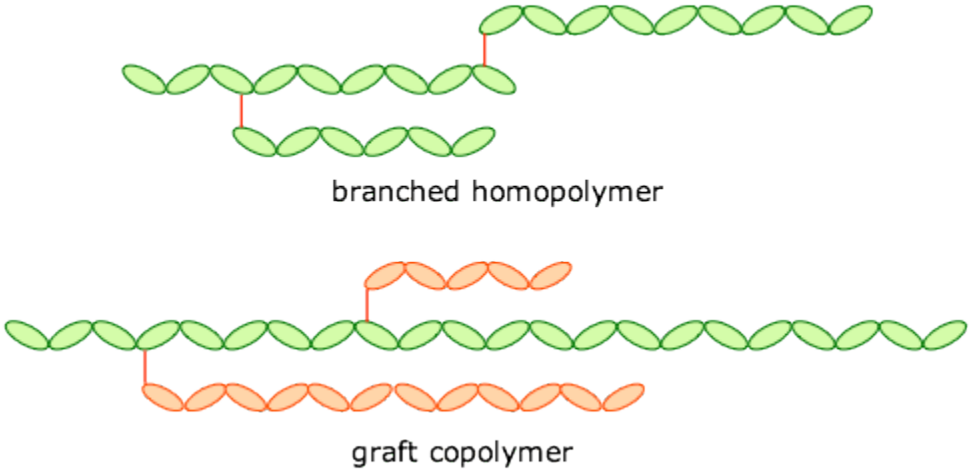


A homopolymer has the same repeating unit. A block copolymer has segments of the chain replaced by another monomer. Alternating copolymer has alternating units of monomer, and a random copolymer has monomer placed in random positions.

A polymer that is composed of identical monomeric units (as is polyethylene) is called a *homopolymer*. *Heteropolymers* are built up from more than one type of monomer. Artificial heteropolymers are more commonly known as copolymers.

Chain topology

Polymers may also be classified as straight-chained or branched, leading to forms such as these:



A branched homopolymer has branches made up of similar monomers while a graft copolymer has branches which are made up of other monomers.

The monomers can be joined end-to-end, and they can also be *cross-linked* to provide a harder material:



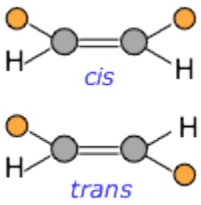
The cross-linked polymer shown here is made up of two similar polymers that are connected to each other through multiple points.

If the cross-links are fairly long and flexible, adjacent chains can move with respect to each other, producing an *elastic* polymer or *elastomer*

Chain configuration and tacticity

In a linear polymer such as polyethylene, rotations around carbon-carbon single bonds can allow the chains to bend or curl up in various ways, resulting in the spaghetti-like mixture of these different *conformations* we alluded to above. But if one of the hydrogen atoms is replaced by some other entity such as a methyl group, the relative orientations of the individual monomer units that make up a linear section of any carbon chain becomes an important characteristic of the polymer.

***Cis-trans* isomerism** occurs because rotation around carbon-carbon double bonds is not possible — unlike the case for single bonds. Any pair of unlike substituents attached to the two carbons is permanently locked into being on the same side (*cis*) or opposite sides (*trans*) of the double bond.



If the carbon chain contains double bonds, then *cis-trans isomerism* becomes possible, giving rise to two different possible

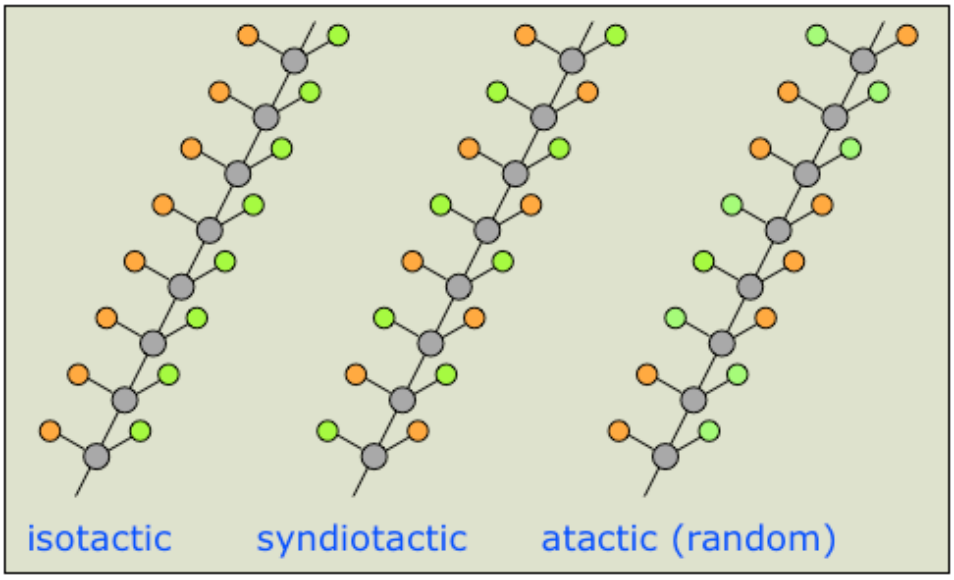
configurations (known as diastereomers) at each unit of the chain. This seemingly small variable can profoundly affect the nature of the polymer. For example, the latex in natural rubber is made mostly of *cis*-polyisoprene, whereas the *trans* isomer (known as gutta percha latex) has very different (and generally inferior) properties.

Chirality

The tetrahedral nature of carbon bonding has an important consequence that is not revealed by simple two-dimensional structural formulas: atoms attached to the carbon can be on one side or on the other, and these will not be geometrically equivalent if all four of the groups attached to a single carbon atom are different. Such carbons (and the groups attached to them) are said to be *chiral,* and can exist in two different three-dimensional forms known as *enantiomers*.

For an individual carbon atom in a polymer chain, two of its attached groups will ordinarily be the chain segments on either side of the carbon. If the two remaining groups are different (say one hydrogen and the other methyl), then the above conditions are satisfied and this part of the chain can give rise to two enantiomeric forms.

A chain that can be represented as (in which the orange and green circles represent different groups) will have multiple chiral centers, giving rise to a huge number of possible enantiomers. In practice, it is usually sufficient to classify chiral polymers into the following three classes of *stereoregularity*, usually referred to as *tacticity*.



In the first chain labeled isotactic, all chircal centers are shown to have the same configuration. For the syndiotactic chain, every other chiral center have the same configuration. In atactic chains, the arrangement of chiral centers are random.

The tacticity of a polymer chain can have a major influence on its properties. Atactic polymers, for example, being more disordered, cannot crystallize.

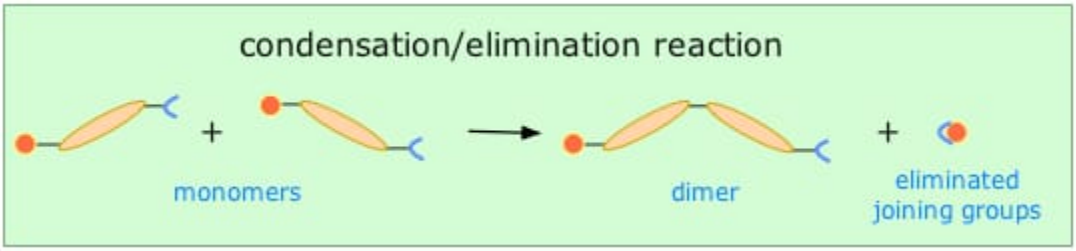
One of the major breakthroughs in polymer chemistry occurred in the early 1950s when the German chemist Karl Ziegler discovered a group of catalysts that could efficiently polymerize ethylene. At about the same time, Giulio Natta (Italian) made the first isotactic (and crystalline) polyethylene. The Ziegler-Natta catalysts revolutionized polymer chemistry by making it possible to control the stereoregularity of these giant molecules. The two shared the 1963 Nobel Prize in Chemistry

3 How polymers are made

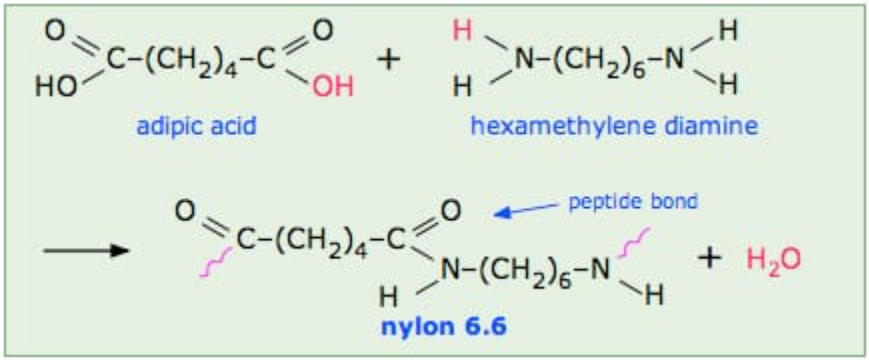
Polymers are made by joining small molecules into large ones. But most of these monomeric molecules are perfectly stable as they are, so chemists have devised two general methods to make them react with each other, building up the backbone chain as the reaction proceeds.

Condensation-elimination polymerization

This method (also known as *step-growth*) requires that the monomers possess two or more kinds of functional groups that are able to react with each other in such a way that parts of these groups combine to form a small molecule (often H_2O) which is eliminated from the two pieces. The now-empty bonding positions on the two monomers can then join together .



This occurs, for example, in the synthesis of the Nylon family of polymers in which the eliminated H_2O molecule comes from the hydroxyl group of the acid and one of the amino hydrogens:

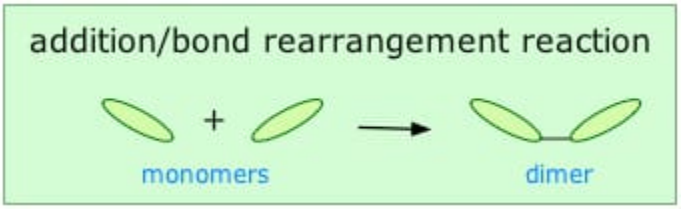


Adipic acid reacts with hexamethylene diamine to form Nylon 6.6 and a H 2 O molecule. The location of the peptide bond in nylon is shown.

Note that the monomeric units that make up the polymer are not identical with the starting components.

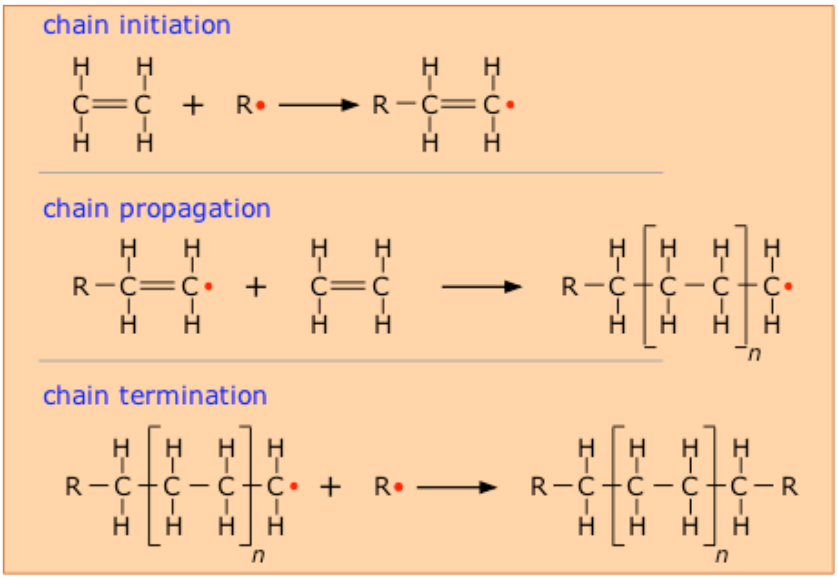
Addition polymerization

Addition or *chain-growth* polymerization involves the rearrangement of bonds within the monomer in such a way that the monomers link up directly with each other:



In order to make this happen, a chemically active molecule (called an *initiator*) is needed to start what is known as a *chain reaction*. The manufacture of polyethylene is a very common example of such a process. It employs a *free-radical* initiator that donates its unpaired electron to the monomer, making the latter highly reactive and able to form a bond with another monomer at this site.

In theory, only a single chain-initiation process needs to take place, and the chain-propagation step then repeats itself indefinitely, but in practice multiple initiation steps are required, and eventually two radicals react (*chain termination*) to bring the polymerization to a halt.



During chain initiation, a free radical reacts with a monomer to make it highly reactive. This monomer is able to make other molecules highly active in the chain propagation step. In the termination step, two radicals react with each other to form a stable molecule.

As with all polymerizations, chains having a range of molecular weights are produced, and this range can be altered by controlling the pressure and temperature of the process.

4 Gallery of common synthetic polymers

Thermoplastics

Note: the left panels below show the polymer name and synonyms, structural formula, glass transition temperature, melting point/ decomposition temperature, and (where applicable) the *resin identification symbol* used to facilitate recycling.

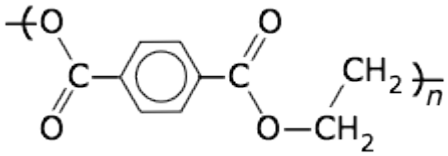
Polycarbonate (Lexan®)



This polymer was discovered independently in Germany and the U.S. in 1953. Lexan is exceptionally hard and strong; we see it most commonly in the form of compact disks. It was once widely used in water bottles, but concerns about leaching of unreacted monomer (bisphenol-A) has largely suppressed this market.

T_g = 145°C, T_m = 225°C.

Polyethylene terephthalate (PET, **Mylar**)



T_g = 76°C, T_m = 250°C.



Thin and very strong films of this material are made by drawing out the molten polymer in both directions, thus orienting the molecules into a highly crystalline state that becomes "locked-in" on cooling. Its many applications include food packaging (in foil-laminated drink containers and microwaveable frozen-food containers), overhead-projector film, weather balloons, and as aluminum-coated reflective material in spacecraft and other applications.

Polycarbonate (Lexan®)



T_g = 145°C, T_m = 225°C.

This polymer was discovered independently in Germany and the U.S. in 1953. Lexan is exceptionally hard and strong; we see it most commonly in the form of compact disks. It was once widely used in water bottles, but concerns about leaching of unreacted monomer (bisphenol-A) has largely suppressed this market.

Nylon (a *polyamide*)



T_g = 50°C, T_m = 255°C.

Nylon has a fascinating history, both scientific and cultural. It was invented by DuPont chemist Wallace Carothers (1896-1937). The common form **Nylon 6.6** has six carbon atoms in both parts of its chain; there are several other kinds. Notice that the two copolymer sub-units are held together by *peptide* bonds, the same kinds that join amino acids into proteins.

Nylon 6.6 has good abrasion resistance and is self-lubricating, which makes it a good engineering material. It is also widely used as a fiber in carpeting, clothing, and tire cord.

For an interesting account of the development of Nylon, see *Enough for One Liftetime: Wallace Carothers, Inventor of Nylon*by Ann Gaines (1971)

Polycarbonate (Lexan®)  **T_g = 145°C, T_m = 225°C.**	**This polymer was discovered independently in Germany and the U.S. in 1953. Lexan is exceptionally hard and strong; we see it most commonly in the form of compact disks. It was once widely used in water bottles, but concerns about leaching of unreacted monomer (bisphenol-A) has largely suppressed this market.**
Polyacrylonitrile (Orlon, Acrilan, "acrylic" fiber)  T_g = 85°C, T_m = 318°C.	Used in the form of fibers in rugs, blankets, and clothing, especially cashmere-like sweaters. The fabric is very soft, but tends to "pill" — i.e., produce fuzz-like blobs. Owing to its low glass transition temperature, it requires careful treatment in cleaning and ironing.

Polycarbonate (Lexan®)



T_g = 145°C, T_m = 225°C.

This polymer was discovered independently in Germany and the U.S. in 1953. Lexan is exceptionally hard and strong; we see it most commonly in the form of compact disks. It was once widely used in water bottles, but concerns about leaching of unreacted monomer (bisphenol-A) has largely suppressed this market.

Polyethylene



T_g = –78°C, T_m = 100°C.

Control of polymerization by means of catalysts and additives has led to a large variety of materials based on polyethylene that exhibit differences in densities, degrees of chain branching and crystallinity, and cross-linking. Some major types are low-density (LDPE), linear low density (LLDPE), high-density (HDPE).

LDPE was the first commercial form (1933) and is used mostly for ordinary "plastic bags", but also for food containers and in six-pack soda can rings. Its low density is due to long-chain branching that inhibits close packing. LLDPE has less branching; its greater toughness allows its use in those annoyingly-thin plastic bags often found in food markets.

A "very low density" form (VLDPE) with extensive short-chain branching is now used for plastic stretch wrap (replacing the original component of Saran Wrap) and in flexible tubing.

HDPE has mostly straight chains and is therefore stronger. It is widely used in milk jugs and similar containers, garbage containers, and as an "engineering plastic" for machine parts.

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LDPE

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HDPE

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Polymethylmethacrylate (Plexiglass, Lucite, Perspex)  T_g = 114°C, T_m = 130-140°C.	This clear, colorless polymer is widely used in place of glass, where its greater impact resistance, lighter weight, and machineability are advantages. It is normally copolymerized with other substances to improve its properties. Aircraft windows, plastic signs, and lighting panels are very common applications. Its compatibility with human tissues has led to various medical applications, such as replacement lenses for cataract patients.

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Polypropylene



T_g = –10°C, T_m = 173°C.

Polypropylene is used alone or as a copolymer, usually with with ethylene. These polymers have an exceptionally wide range of uses — rope, binder covers, plastic bottles, staple yarns, non-woven fabrics, electric kettles. When uncolored, it is translucent but not transparent. Its resistance to fatigue makes it useful for food containers and their lids, and flip-top lids on bottled products such as ketchup.

Polycarbonate (Lexan®)



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PP

Polycarbonate (Lexan®)



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polystyrene



T_g = 95°C, T_m = 240°C.

Polystyrene is transparent but rather brittle, and yellows under uv light.

Widely used for inexpensive packaging materials and "take-out trays", foam "packaging peanuts", CD cases, foam-walled drink cups, and other thin-walled and moldable parts.

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T_g = 145°C, T_m = 225°C.



PS

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polyvinyl acetate  T_g = 30°C	PVA is too soft and low-melting to be used by itself; it is commonly employed as a water-based emulsion in paints, wood glue and other adhesives.

Polycarbonate (Lexan®)



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polyvinyl chloride ("vinyl", "PVC")



T_g = 85°C, T_m = 240°C.

This is one of the world's most widely used polymers. By itself it is quite rigid and used in construction materials such as pipes, house siding, flooring. Addition of plasticizers make it soft and flexible for use in upholstery, electrical insulation, shower curtains and waterproof fabrics. There is some effort being made to phase out this polymer owing to environmental concerns (see below).

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T_g = 145°C, T_m = 225°C.



PVC

Polycarbonate (Lexan®)



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Synthetic rubbers

Neoprene (polychloroprene)
T_g = –70°C



Polybutadiene T_g < –90°C

Neoprene, invented in 1930, was the first mass-produced synthetic rubber. It is used for such things as roofing membranes and wet suits.

Polybutadiene substitutes a hydrogen for the chlorine; it is the major component (usually admixed with other rubbers) of tires. Synthetic rubbers played a crucial role in World War II

SBS (styrene-butadiene-styrene) rubber is a block copolymer whose special durability makes it valued for tire treads.

Polycarbonate (Lexan®)



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Polytetrafluroethylene (**Teflon**, PTFE)



This highly-crystalline fluorocarbon is exceptionally inert to chemicals and solvents. Water and oils do not wet it, which accounts for its use in cooking ware and other anti-stick applications, including personal care products.

These properties — non-adhesion to other materials, non-wetability, and very low coefficient of friction ("slipperyness") — have their origin in the highly electronegative nature of fluorine whose atoms partly shield the carbon chain. Fluorine's outer electrons are so strongly attracted to its nucleus that they are less available to participate in London (dispersion force) interactions.

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T_g = 145°C, T_m = 225°C.



Decomposes above 350°C.

Polycarbonate (Lexan®)



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Polyaramid (Kevlar)



Sublimation temperature 450°C.

Kevlar is known for its ability to be spun into fibers that have five times the tensile strength of steel. It was first used in the 1970s to replace steel tire cords. Bullet-proof vests are one of it more colorful uses, but other applications include boat hulls, drum heads, sports equipment, and as a replacement for asbestos in brake pads. It is often combined with carbon or glass fibers in composite materials.

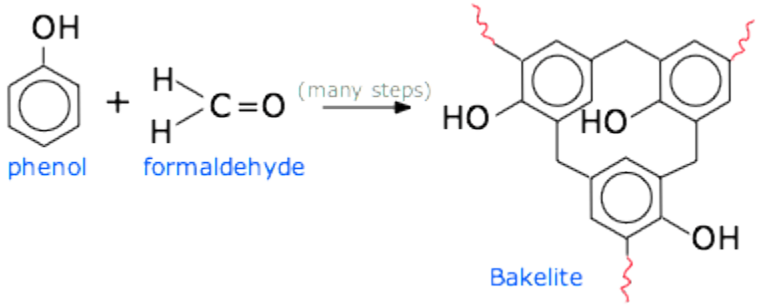
The high tensile strength is due in part to the extensive hydrogen bonding between adjacent chains.

Kevlar also has the distinction of having been invented by a woman chemist, Stephanie Kwolek.

Thermosets

The thermoplastic materials described above are chains based on relatively simple monomeric units having varying degrees of polymerization, branching, bending, cross-linking and crystallinity, but with each molecular chain being a discrete unit. In thermosets, the concept of an individual molecular unit is largely lost; the material becomes more like a gigantic extended molecule of its own — hence the lack of anything like a glass transition temperature or a melting point.

These properties have their origins in the nature of the monomers used to produce them. The most important feature is the presence of multiple reactive sites that are able to form what amount to cross-links at every center. The phenolic resins, typified by the reaction of phenol with formaldehyde, illustrate the multiplicity of linkages that can be built.



Phenolic resins



These are made by condensing one or more types of phenols (hydroxy-substituted benzene rings) with formaldehyde, as illustrated above. This was the first commercialized synthetic molding plastic. It was developed in 1907-1909 by the Belgian chemist Leo Baekeland, hence the common name bakelite. The brown material (usually bulked up with wood powder) was valued for its electrical insulating properties (light fixtures, outlets and other wiring devices) as well as for consumer items prior to the mid-century. Since that time, more recently developed polymers have largely displaced these uses. Phenolics are still extensively used as adhesives in plywood manufacture, and for making paints and varnishes.

Urea resins



Condensation of formaldehyde with urea yields lighter-colored and less expensive materials than phenolics. The major use if urea-formaldehyde resins is in bonding wood particles into particle board. Other uses are as baked-on enamel coatings for kitchen appliances and to coat cotton and rayon fibers to impart wrinkle- water-, and stain-resistance to the finished fabrics.

Melamine resins



Melamine, with even more amino ($-NH_2$) groups than urea, reacts with formaldehyde to form colorless solids that are harder then urea resins. The are most widely encountered in dinner-ware (plastic plates, cups and serving bowls) and in plastic laminates such as Formica.

Alkyd-polyester resins

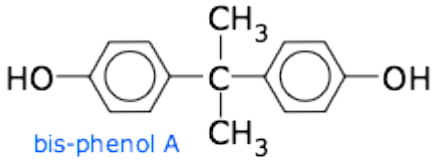


An ester is the product of the reaction of an organic acid with an alcohol, so polyesters result when multifunctional acids such as phthalic acid react with polyhydric alcohols such as glycerol. The term *alkyd* derives from the two words alcohol and acid.

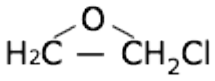
Alkyd resins were first made by Berzelius in 1847, and they were first commercialized as ***Glyptal*** (glycerine + phthalic acid) varnishes for the paint industry in 1902.

The later development of other polyesters greatly expanded their uses into a wide variety of fibers and molded products, ranging from clothing fabrics and pillow fillings to glass-reinforced plastics.

Epoxy resins



bis-phenol A



epichlorohydrin

This large and industrially-important group of resins typically starts by condensing bisphenol-A with epichlorohydrin in the presence of a catalyst. (The *-epi*prefix refers to the *epoxide* group in which an oxygen atom that bridges two carbons.) These resins are usually combined with others to produce the desired properties. Epoxies are especially valued as glues and adhesives, as their setting does not depend on evaporation and the setting time can be varied over a wide range. In the *two-part resins* commonly sold for home use, the unpolymerized mixture and the hardener catalyst are packaged separately for mixing just prior to use. In some formulations the polymerization is initiated by heat ("heat curing"). Epoxy *dental fillings* are cured by irradiation with uv light.

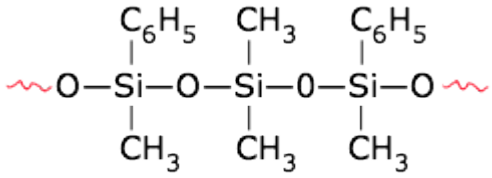
Polyurethanes



Organic isocyanates R–NCO react with multifunctional alcohols to form polymeric *carbamates*, commonly referred to as *polyurethanes*. Their major use is in plastic foams for thermal insulation and upholstery, but a very large number of other applications, including paints and varnishes and plastic wheels used in fork-lift trucks, shopping carts and skateboards.

Silicones

Polysiloxanes (–Si–O–Si-) are the most important of the small class *inorganic polymers*. The commercial silicone polymers usually contained attached organic side groups that aid to cross-linking. Silicones can be made in a wide variety of forms; those having lower molecular weights are liquids, while the more highly polymerized materials are rubbery solids. These polymers have a similarly wide variety of applications: lubricants, caulking materials and sealants, medical implants, non-stick cookware coatings, hair-conditioners and other personal-care products.



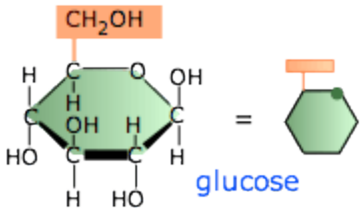
a typical silicone polymer

Natural Polymers

Polymers derived from plants have been essential components of human existence for thousands of years. In this survey we will look at only those that have major industrial uses, so we will not be discussing the very important biopolymers *proteins* and *nucleic acids*.

Polysaccharides

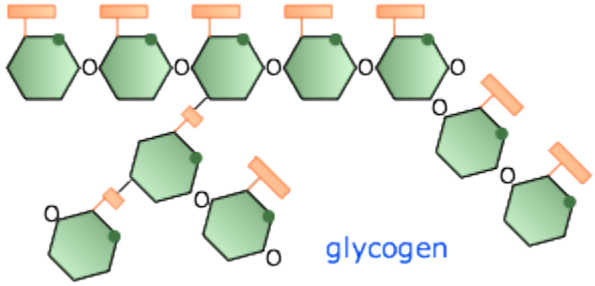
Polysaccharides are polymers of *sugars*; they play essential roles in energy storage, signaling, and as structural components in all living organisms. The only ones we will be concerned with here are those composed of *glucose*, the most important of the six-carbon *hexoses*. Glucose serves as the primary fuel of most organisms.



Glucose, however, is highly soluble and cannot be easily stored, so organisms make polymeric forms of glucose to set aside as *reserve storage*, from which glucose molecules can be withdrawn as needed.

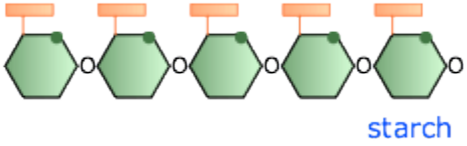
Glycogen

In humans and higher animals, the reserve storage polymer is *glycogen*. It consists of roughly 60,000 glucose units in a highly branched configuration. Glycogen is made mostly in the liver under the influence of the hormone *insulin* which triggers a process in which digested glucose is polymerized and stored mostly in that organ. A few hours after a meal, the glucose content of the blood begins to fall, and glycogen begins to be broken down in order to maintain the body's required glucose level.



Starch

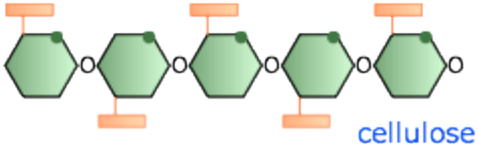
In plants, these glucose-polymer reserves are known as *starch*. Starch granules are stored in seeds or tubers to provide glucose for the energy needs of newly-germinated plants, and in the twigs of deciduous plants to tide them over during the winter when *photosynthesis* (the process in which glucose is synthesized from CO_2 and H_2O) does not take place. The starches in food grains such as rice and wheat, and in tubers such as potatoes, are a major nutritional source for humans.



Plant starches are mixtures of two principal forms, *amylose* and *amylopectin*. Amylose is a largely-unbranched polymer of 500 to 20,000 glucose molecules that curls up into a helical form that is stabilized by internal hydrogen bonding. Amylopectin is a much larger polymer having up to two million glucose residues arranged into branches of 20 to 30 units.

Cellulose and its derivatives

Cellulose is the most abundant organic compound on the earth. Extensive hydrogen bonding between the chains causes native cellulose to be about 70% crystalline. It also raises the melting point (>280°C) to above its combustion temperature. The structures of starch and cellulose appear to be very similar; in the latter, every other glucose molecule is "upside-down". But the consequences of this are far-reaching; starch can dissolve in water and can be digested by higher animals including humans, whereas cellulose is insoluble and undigestible. Cellulose serves as the principal structural component of green plants and (along with lignin) in wood.





Cotton is one of the purest forms of cellulose and has been cultivated since ancient times. Its ability to absorb water (which increases its strength) makes cotton fabrics especially useful for clothing in very warm climates.

Cotton also serves (along with treated wood pulp) as the source the industrial production of cellulose-derived materials which were the first "plastic" materials of commercial importance.

- Nitrocellulose was developed in the latter part of the 19th Century. It is prepared by treating cotton with nitric acid, which reacts with the hydroxyl groups in the cellulose chain. It was first used to make molded objects the first material used for a photographic film base by Eastman Kodak. Its extreme flammability posed considerable danger in movie theaters, and its spontaneous slow decomposition over time had seriously degraded many early films before they were transferred to more stable media. Nitrocellulose was also used as an explosive and propellant, for which applications it is known as *guncotton*.
- **Cellulose acetate** was developed in the early 1900s and became the first artificial fiber that was woven into fabrics that became prized for their lustrous appearance and wearing comfort. Kodak developed it as a "safety film" base in the 1930's to replace nitrocellulose, but it did not come into wide use for this purpose until 1948. A few years later, is became the base material for magnetic recording tape.
-  **Viscose** is the general term for "regenerated" forms of cellulose made from solutions

of the polymer in certain strong solvents. When extruded into a thin film it becomes cellophane which has been used as a food wrapping since 1912 and is the base for transparent adhesive tapes such as Scotch Tape. Viscose solutions extruded through a spinneret produce fibers known as rayon. Rayon (right) was the first "artificial silk" and has been used for tire cord, apparel, and carpets. It was popular for womens' stockings before Nylon became available for this purpose.

Rubber



A variety of plants produce a sap consisting of a colloidal dispersion of *cis*-polyisoprene. This milky fluid is especially abundant in the rubber tree (*Hevea*), from which it drips when the bark is wounded. After collection, the latex is coagulated to obtain the solid rubber. Natural rubber is thermoplastic, with a glass transition temperature of –70°C.



cis-polyisoprene

Raw natural rubber tends to be sticky when warm and brittle when cold, so it was little more than a novelty material when first introduced to Europe around 1770. It did not become generally useful until the mid-nineteenth century when Charles Goodyear found that heating it with sulfur — a process he called *vulcanization* — could greatly improve its properties.



Why does a rubber band heat up when it is stretched, and why does it spontaneously snap back? It all has to do with *entropy*.

Vulcanization creates disulfide cross-links that prevent the polyisoprene chains from sliding over each other. The degree of cross-linking can be controlled to produce a rubber having the desired elasticity and hardness. More recently, other kinds of chemical treatment (such as epoxidation) have been developed to produce rubbers for special purposes.

Better things for better living... through chemistry" is a famous commercial slogan that captured the attitude of the public around 1940 when synthetic polymers were beginning to make a major impact in people's lives. What was not realized at the time, however, were some of the problems these materials would create as their uses multiplied and the world became more wary of "chemicals". (DuPont dropped the "through chemistry" part in 1982.)

Small-molecule release

Many kinds of polymers contain small molecules — either unreacted monomers, or substances specifically added (plasticizers, uv absorbers, flame retardants, etc.) to modify their properties. Many of these smaller molecules are able to diffuse through the material and be released into any liquid or air in contact with the plastic — and eventually into the aquatic environment. Those that are used for building materials (in mobile homes, for example) can build up in closed environments and contribute to indoor air pollution.

Residual monomer

Formation of long polymer chains is a complicated and somewhat random process that is never perfectly stoichiometric. It is therefore not uncommon for some unreacted monomer to remain in the finished product. Some of these monomers, such as formaldehyde, styrene (from polystyrene, including polystyrene foam food take-out containers), vinyl chloride, and bisphenol-A (from polycarbonates) are known carcinogens. Although there is little evidence that the small quantities that diffuse into the air or leach out into fluids pose a quantifiable health risk, people are understandably reluctant to tolerate these exposures, and public policy is gradually beginning to regulate them.

Perfluorooctanoic acid (PFOA), the monomer from which Teflon is made, has been the subject of a 2004 lawsuit against a DuPont factory that contaminated groundwater. Small amounts of PFOA have been detected in gaseous emissions from hot fluorocarbon products.

Plasticizers



These substances are compounded into certain types of plastics to render them more flexible by lowering the glass transition temperature. They accomplish this by taking up space between the polymer chains and acting as lubricants to enable the chains to more readily slip over each other. Many (but not all) are small enough to be diffusible and a potential source of health problems.

Polyvinyl chloride polymers are one of the most widely-plasticized types, and the odors often associated with flexible vinyl materials such as garden hoses, waterbeds, cheap shower curtains, raincoats and upholstery are testament to their ability to migrate into the environment.

The well-known "new car smell" is largely due to plasticizer release from upholstery and internal trim.

There is now an active movement to develop non-diffusible and "green" plasticizers that do not present these dangers.

Endocrine disrupters

> Plastics-related compounds are not the only kind of endocrine disrupters found in the environment. Others include pesticide and fungicide residues, and industrial chemicals such as polychlorinated biphenols (PCBs).

To complicate matters even further, many of these small molecules have been found to be physiologically active owing to their ability to mimic the action of hormones or other signaling molecules, probably by fitting into and binding with the specialized receptor sites present in many tissues. The evidence that many of these chemicals are able to act in this way at the cellular level is fairly clear, but there is still some dispute whether many of these pose actual health risks to adult humans at the relatively low concentrations in which they commonly occur in the environment.

There is, however, some concern about the effects of these substances on non-adults and especially on fetuses, given that endocrines are intimately connected with sexual differentiation and neurological development which continues up through the late teens.

Decomposition products

Most commonly-used polymers are not readily biodegradable, particularly under the anaerobic conditions of most landfills. And what decomposition does occur will combine with rainwater to form *leachate*s that can contaminate nearby streams and groundwater supplies. Partial photodecomposition, initiated by exposure to sunlight, is a more likely long-term fate for exposed plastics, resulting in tiny broken-up fragments. Many of these materials are less dense than seawater, and once they enter the oceans through coastal sewage outfalls or from marine vessel wastes, they tend to remain there indefinitely.

Open burning of polymeric materials containing chlorine (polyvinyl chloride, for example) is known to release compounds such

as dioxins that persist in the environment. Incineration under the right conditions can effectively eliminate this hazard.

Disposed products containing **fluorocarbons** (Teflon-coated ware, some personal-care, waterproofing and anti-stick materials) break down into perfluorooctane sulfonate which has been shown to damage aquatic animals.

Hazards to animals

There are two general types of hazards that polymers can introduce into the aquatic environment. One of these relates to the release of small molecules that act as hormone disrupters as described above. It is well established that small aquatic animals such as fish are being seriously affected by such substances in many rivers and estuarine systems, but details of the sources and identities of these molecules have not been identified. One confounding factor is the release of sewage water containing human birth-control drugs (which have a feminizing effect on sexual development) into many waterways.

The other hazard relates to pieces of plastic waste that aquatic animals mistake for food or become entangled in.



This plastic bag (probably mistaken for a jellyfish, the sea turtle's only food) cannot be regurgitated and leads to intestinal blockage and a slow death.



Remains of an albatross that mistook bits of plastic junk for food

These dangers occur throughout the ocean, but are greatly accentuated in regions known as gyres. These are regions of the ocean in which a combination of ocean currents drives permanent vortices that tend to collect and concentrate floating materials. The most notorious of these are the Great Pacific Gyres that have accumulated astounding quantities of plastic waste.



Recycling



The huge quantity (one estimate is 10^8 metric tons per year) of plastic materials produced for consumer and industrial use has created a gigantic problem of what to do with plastic waste which is difficult to incinerate safely and which, being largely non-biodegradable, threatens to overwhelm the capacity of landfills. An additional consideration is that *de novo* production most of the major polymers consumes non-renewable hydrocarbon resources.

Plastic water bottles (left) present a special recycling problem because of their widespread use in away-from-home locations.

Plastics recycling has become a major industry, greatly aided by enlightened trash management policies in the major developed nations. However, it is plagued with some special problems of its own:

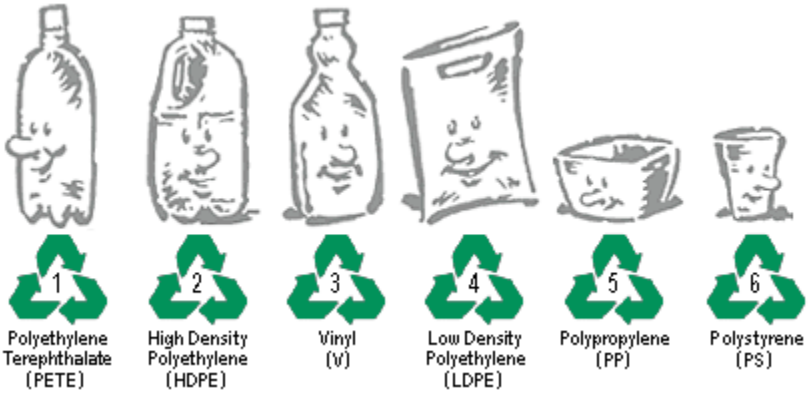
- Recycling is only profitable when there is a market for the regenerated material. Such markets vary with the economic cycle (they practically disappeared during the recession that commenced in 2008.)
- The energy-related costs of collecting and transporting plastic waste, and especially of processing it for re-use, are frequently the deciding factor in assessing the practicability of recycling.
- Collection of plastic wastes from diverse sources and locations and their transport to processing centers consumes energy and presents numerous operational problems.
- Most recycling processes are optimized for particular classes of polymers. The diversity of plastic types necessitates their

separation into different waste streams — usually requiring manual (i.e., low-cost) labor. This in turn encourages shipment of these wastes to low-wage countries, thus reducing the availability of recycled materials in the countries in which the plastics originated.

Some of the major recycling processes include

- Thermal decomposition processes that can accommodate mixed kinds of plastics and render them into fuel oil, but the large inputs of energy they require have been a problem.
- A very small number of condensation polymers can be depolymerized so that the monomers can be recovered and re-used.
- Thermopolymers can be melted and pelletized, but those of widely differing types must be treated separately to avoid incompatability problems.
- Thermosets are usually shredded and used as filler material in recycled thermopolymers.

In order to facilitate efficient recycling, a set of seven *resin idenfication codes* has been established (the seventh, not shown below, is "other").



1. Polyethylene Terephthalate (PETE) 2. High density polyethylene (HDPE) 3. Vinyl (V) 4. Low density polyethylene (LDPE) 5. Polypropylene (PP) 6. Polystyrene. (PS)

These codes are stamped on the bottoms of many containers of widely-distributed products. Not all categories are accepted by all local recycling authorities, so residents need to be informed about which kinds should be placed in recycling containers and which should be combined with ordinary trash.

Tire recycling

The large number of rubber tires that are disposed of, together with the increasing reluctance of landfills to accept them, has stimulated considerable innovation in the re-use of this material, especially in the construction industry.

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12.3: MATERIALS FOR MEDICINE

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12.3.1: Anti-Cancer Drugs I

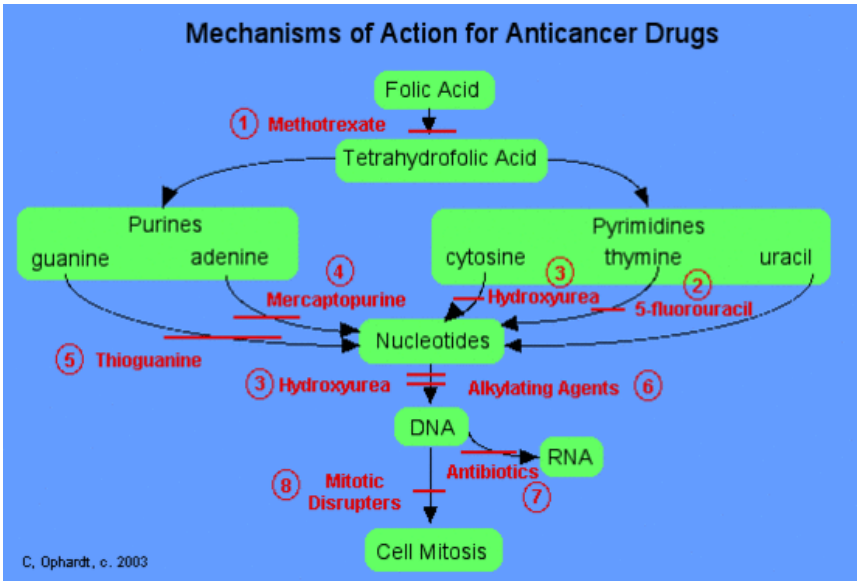
The available anticancer drugs have distinct mechanisms of action which may vary in their effects on different types of normal and cancer cells. A single "cure" for cancer has proved elusive since there is not a single type of cancer but as many as 100 different types of cancer. In addition, there are very few demonstrable biochemical differences between cancerous cells and normal cells. For this reason the effectiveness of many anticancer drugs is limited by their toxicity to normal rapidly growing cells in the intestinal and bone marrow areas. A final problem is that cancerous cells which are initially suppressed by a specific drug may develop a resistance to that drug. For this reason cancer chemotherapy may consist of using several drugs in combination for varying lengths of time.

Introduction

Chemotherapy drugs, are sometimes feared because of a patient's concern about toxic effects. Their role is to slow and hopefully halt the growth and spread of a cancer. There are three goals associated with the use of the most commonly-used anticancer agents.

1. Damage the DNA of the affected cancer cells.
2. Inhibit the synthesis of new DNA strands to stop the cell from replicating, because the replication of the cell is what allows the tumor to grow.
3. Stop mitosis or the actual splitting of the original cell into two new cells. Stopping mitosis stops cell division (replication) of the cancer and may ultimately halt the progression of the cancer.

Unfortunately, the majority of drugs currently on the market are not specific, which leads to the many common side effects associated with cancer chemotherapy. Because the common approach of all chemotherapy is to decrease the growth rate (cell division) of the cancer cells, the side effects are seen in bodily systems that naturally have a rapid turnover of cells iincluding skin, hair, gastrointestinal, and bone marrow. These healthy, normal cells, also end up damaged by the chemotherapy program.



Categories of Chemotherapy Drugs

In general, chemotherapy agents can be divided into three main categories based on their mechanism of action.

- **Stop the synthesis of pre DNA molecule building blocks**

These agents work in a number of different ways. DNA building blocks are folic acid, heterocyclic bases, and nucleotides,

which are made naturally within cells. All of these agents work to block some step in the formation of nucleotides or deoxyribonucleotides (necessary for making DNA). When these steps are blocked, the nucleotides, which arethe building blocks of DNA and RNA, can not be synthesized. Thus the cells can not replicate because they can nnot make DNA without the nucleotides. Examples of drugs in this class include 1) methotrexate (Abitrexate®),2) fluorouracil (Adrucil®), 3) hydroxyurea (Hydrea®), and 4) mercaptopurine (Purinethol®).

- **Directly damage the DNA in the nucleus of the cell**

These agents chemically damage DNA and RNA. They disrupt replication of the DNA and either totally halt replication or cause the manufacture of nonsense DNA or RNA (i.e. the new DNA or RNA does not code for anything useful). Examples of drugs in this class include cisplatin (Platinol®) and 7) antibiotics - daunorubicin (Cerubidine®), doxorubicin (Adriamycin®), and etoposide (VePesid®).

- **Effect the synthesis or breakdown of the mitotic spindles**

Mitotic spindles serve as molecular railroads with "North and South Poles" in the cell when a cell starts to divide itself into two new cells. These spindles are very important because they help to split the newly copied DNA such that a copy goes to each of the two new cells during cell division. These drugs disrupt the formation of these spindles and therefore interrupt cell division. Examples of drugs in this class of 8) miotic disrupters include: Vinblastine (Velban®), Vincristine (Oncovin®) and Pacitaxel (Taxol®).

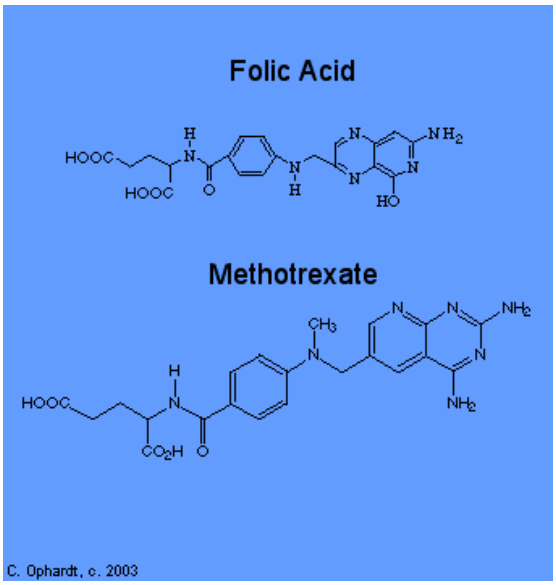
Enzyme L-asparaginase

In the 1950's a biochemical difference in metabolism related to the amino acid asparagine was found. Normal cells apparently can synthesize asparagine while leukemia cells cannot. If leukemia cells are deprived of asparagine, they will eventually die. In an almost unrecognized and parallel discovery, it was found that blood serum from guinea pigs and other South American rodents had antileukemia properties. The enzyme L-asparaginase was eventually identified as the anticancer agent. L-asparaginase was isolated and tested successfully on human leukemias. Eventually the enzyme asparaginase was also found and isolated from the bacteria, E. coli.

If the enzyme L-asparaginase is given to humans, various types of leukemias can be controlled. Tumor cells, more specifically lymphatic tumor cells, require huge amounts of asparagines to keep up with their rapid, malignant growth. This means they use both asparagine from the diet as well as what they can make themselves (which is limited) to satisfy their large asparagines demand. L-asparaginase is an enzyme that destroys asparagine external to the cell. Normal cells are able to make all the asparagine they need internally whereas tumor cells become depleted rapidly and die.The enzyme converts asparagine in the blood into aspartic acid by a deamination reaction. The leukemia cells are thus deprived of their supply of asparagine and will die.

Methotrexate

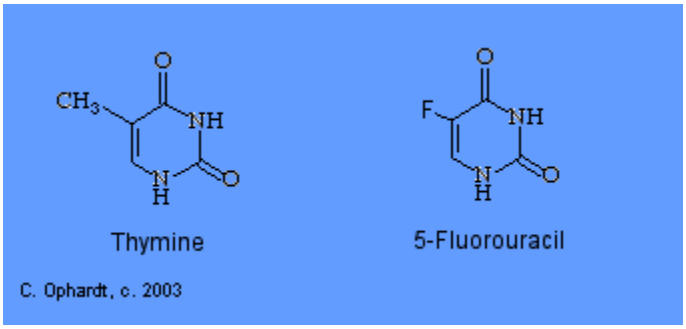
Methotrexate inhibits folic acid reductase which is responsible for the conversion of folic acid to tetrahydrofolic acid. At two stages in the biosynthesis of purines (adenine and guanine) and at one stage in the synthesis of pyrimidines (thymine, cytosine, and uracil), one-carbon transfer reactions occur which require specific coenzymes synthesized in the cell from tetrahydrofolic acid.



Tetrahydrofolic acid itself is synthesized in the cell from folic acid with the help of an enzyme, folic acid reductase. Methotrexate looks a lot like folic acid to the enzyme, so it binds to it thinking that it is folic acid. In fact, methotrexate looks so good to the enzyme that it binds to it quite strongly and inhibits the enzyme. Thus, DNA synthesis cannot proceed because the coenzymes needed for one-carbon transfer reactions are not produced from tetrahydrofolic acid because there is no tetrahydrofolic acid. Again, without DNA, no cell division.

5-Fluorouracil

5-Fluorouracil (5-FU; Adrucil®, Fluorouracil, Efudex®, Fluoroplex®) is an effective pyrimidine antimetabolite. Fluorouracil is synthesized into the nucleotide, 5-fluoro-2-deoxyuridine. This product acts as an antimetabolite by inhibiting the synthesis of 2-deoxythymidine because the carbon - fluorine bond is extremely stable and prevents the addition of a methyl group in the 5-position. The failure to synthesize the thymidine nucleotide results in little or no production of DNA. Two other similar drugs include: gemcitabine (Gemzar®) and arabinosylcytosine (araC). They all work through similar mechanisms.



Contributors

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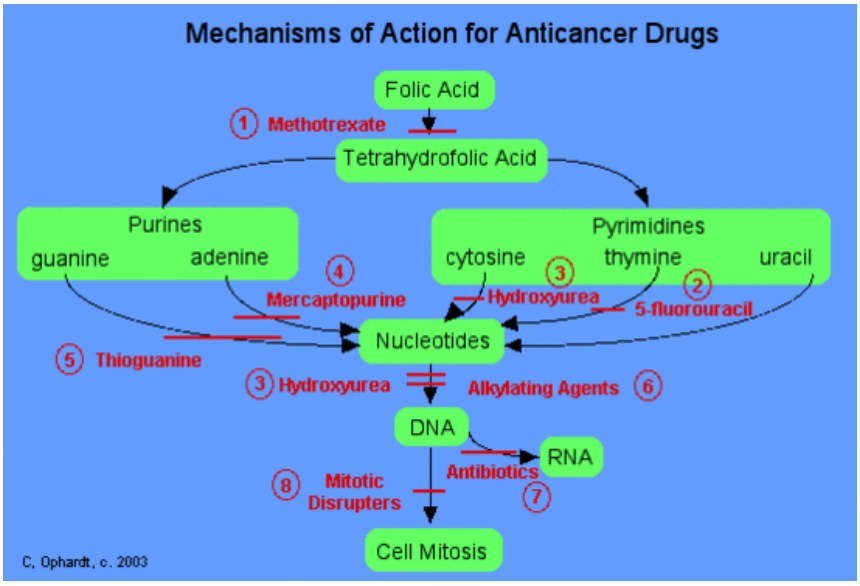
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12.3.2: Anti-Cancer Drugs II

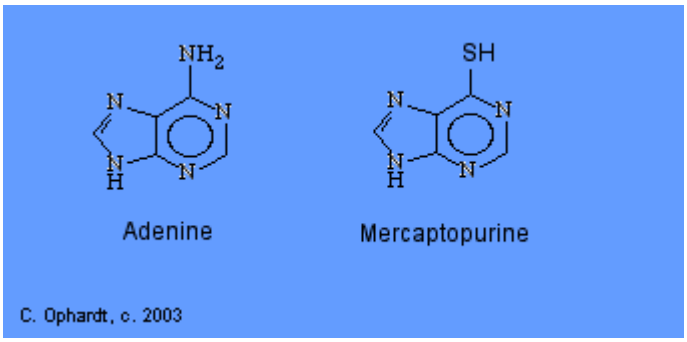
Hydroxyurea

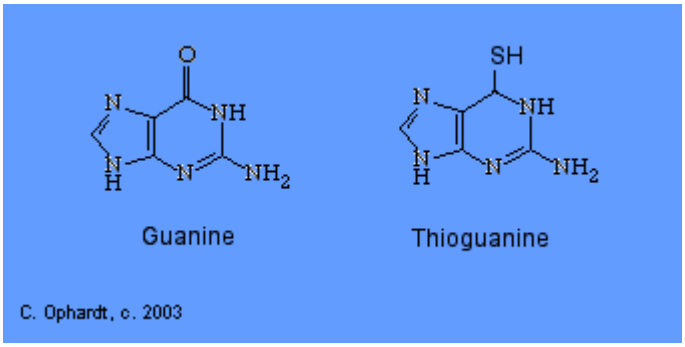
Hydroxyurea blocks an enzyme which converts the cytosine nucleotide into the deoxy derivative. In addition, DNA synthesis is further inhibited because hydroxyurea blocks the incorporation of the thymidine nucleotide into the DNA strand.



Mercaptopurine

Mercaptopurine, a chemical analog of the purine adenine, inhibits the biosynthesis of adenine nucleotides by acting as an antimetabolite. In the body, 6-MP is converted to the corresponding ribonucleotide. 6-MP ribonucleotide is a potent inhibitor of the conversion of a compound called inosinic acid to adenine Without adenine, DNA cannot be synthesized. 6-MP also works by being incorporated into nucleic acids as thioguanosine, rendering the resulting nucleic acids (DNA, RNA) unable to direct proper protein synthesis.





Thioguanine

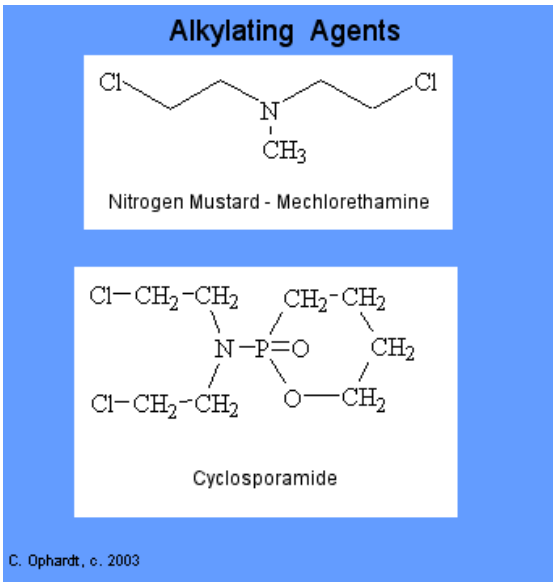
Thioguanine is an antimetabolite in the synthesis of guanine nucleotides.

Alkylating Agents

Alkylating agents involve reactions with guanine in DNA. These drugs add methyl or other alkyl groups onto molecules where they do not belong. This in turn inhibits their correct utilization by base pairing and causes a miscoding of DNA.

1. In the first mechanism an alkylating agent attaches alkyl groups to DNA bases. This alteration results in the DNA being fragmented by repair enzymes in their attempts to replace the alkylated bases.
2. A second mechanism by which alkylating agents cause DNA damage is the formation of cross-bridges, bonds between atoms in the DNA. In this process, two bases are linked together by an alkylating agent that has two DNA binding sites. Cross-linking prevents DNA from being separated for synthesis or transcription.
3. The third mechanism of action of alkylating agents causes the mispairing of the nucleotides leading to mutations.

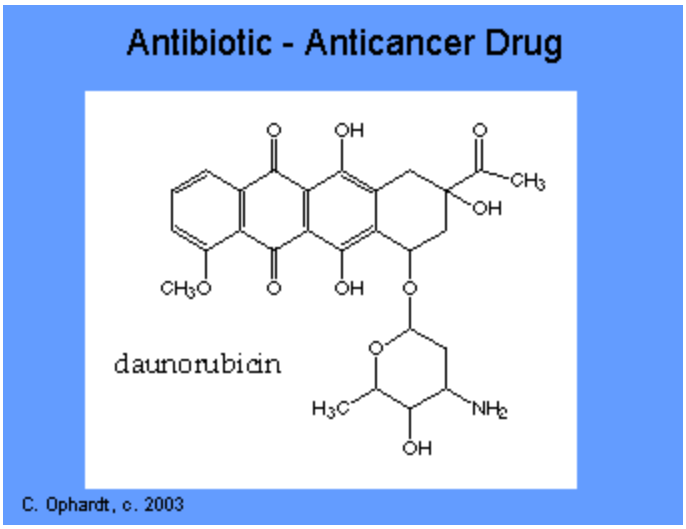
There are six groups of alkylating agents: nitrogen mustards; ethylenimes; alkylsulfonates; triazenes; piperazines; and nitrosureas. Cyclosporamide is a classical example of the role of the host metabolism in the activation of an alkylating agent and is one or the most widely used agents of this class. It was hoped that the cancer cells might posses enzymes capable of accomplishing the cleavage, thus resulting in the selective production of an activated nitrogen mustard in the malignant cells. Compare the top and bottom structures in the graphic on the left.

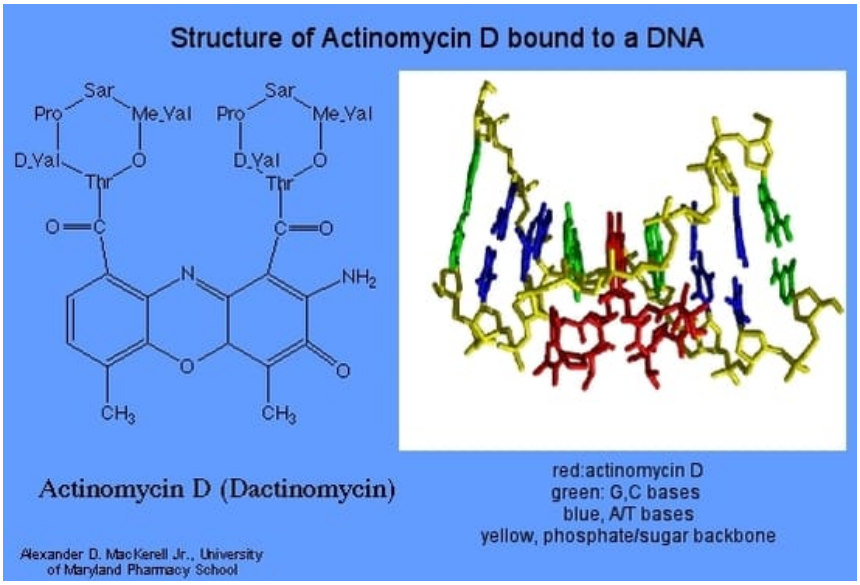


Antibiotics

A number of antibiotics such as anthracyclines, dactinomycin, bleomycin, adriamycin, mithramycin, bind to DNA and inactivate it. Thus the synthesis of RNA is prevented. General properties of these drugs include: interaction with DNA in a variety of different ways including intercalation (squeezing between the base pairs), DNA strand breakage and inhibition with the enzyme topoisomerase II. Most of these compounds have been isolated from natural sources and antibiotics. However, they lack the specificity of the antimicrobial antibiotics and thus produce significant toxicity.

The **anthracyclines** are among the most important antitumor drugs available. Doxorubicin is widely used for the treatment of several solid tumors while **daunorubicin** and idarubicin are used exclusively for the treatment of leukemia. These agents have a number of important effects including: intercalating (squeezing between the base pairs) with DNA affecting many functions of the DNA including DNA and RNA synthesis. Breakage of the DNA strand can also occur by inhibition of the enzyme topoisomerase II.



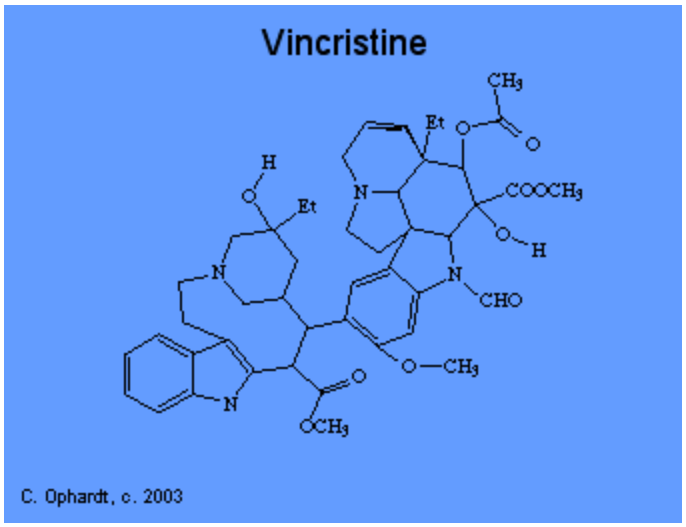


Dactinomycin (Actinomycin D)

At low concentrations dactinomycin inhibits DNA directed RNA synthesis and at higher concentrations DNA synthesis is also inhibited. All types of RNA are affected, but ribosomal RNA is more sensitive. Dactinomycin binds to double stranded DNA , permitting RNA chain initiation but blocking chain elongation. Binding to the DNA depends on the presence of guanine.

Mitotic Disrupters

Plant alkaloids like **vincristine** prevent cell division, or mitosis. There are several phases of mitosis, one of which is the metaphase. During metaphase, the cell pulls duplicated DNA chromosomes to either side of the parent cell in structures called "spindles". These spindles ensure that each new cell gets a full set of DNA. Spindles are microtubular fibers formed with the help of the protein "tubulin". Vincristine binds to tubulin, thus preventing the formation of spindles and cell division.

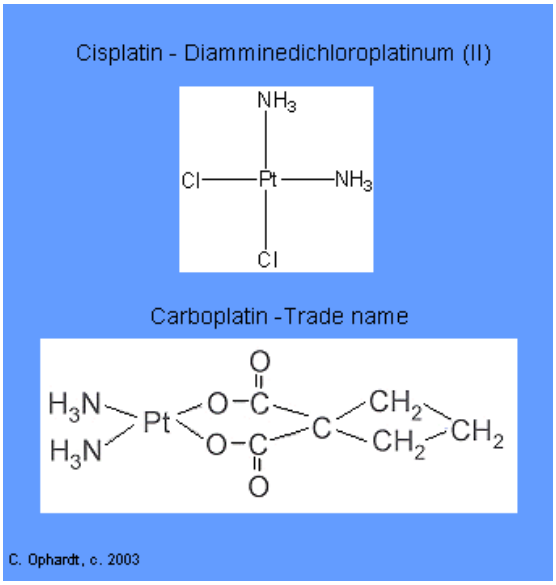


Taxol

Paclitaxel (taxol) was first isolated from the from the bark of the Pacific Yew (Taxus brevifolia). Docetaxel is a more potent analog that is produced semisynthetically. In contrast to other microtubule antagonists, taxol disrupts the equilibrium between free tubulin and mircrotubules by shifting it in the direction of assembly, rather than disassembly. As a result, taxol treatment causes both the stabilization of microtubules and the formation of abnormal bundles of microtubules. The net effect is still the disruption of mitosis.

Mechanism of Intercalating Agents

Intercalating agents wedge between bases along the DNA. The intercalated drug molecules affect the structure of the DNA, preventing polymerase and other DNA binding proteins from functioning properly. The result is prevention of DNA synthesis, inhibition of transcription and induction of mutations. Examples include: **Carboplatin and Cisplatin.**



These related drugs covalently bind to DNA with preferential binding to the N-7 position of guanine and adenine. They are able to bind to two different sites on DNA producing cross-links, either intrastrand (within the same DNA molecule which results in inhibition of DNA synthesis and transcription.

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12.3.3: Antidepressants

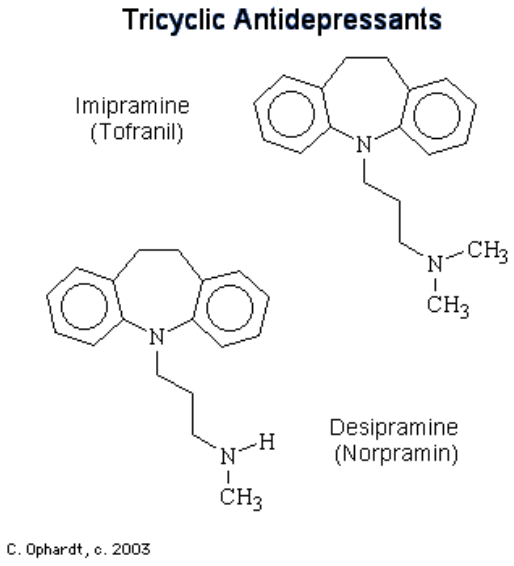
Antidepressant drugs are used to restore mentally depressed patients to an improved mental status. Depression results from a deficiency of norepinephrine at receptors in the brain. Mechanisms that increase their effective concentration at the receptor sites should alleviate depression. Antidepressant drugs act by one or more of the following stimulation type mechanisms:

1. Increase release of norepinephrine: Amphetamines and electroconvulsive therapy act by this mechanism. Amphetamines mimic norepinephrine.
2. Prevent inactivation of norepinephrine:Monoamine oxidase (MAO) inhibitors are thought to act as antidepressant agents in part by preventing the breakdown and inactivation of norepinephrine.
3. Prevent the re uptake of norepinephrine:The action of norepinephrine at the receptor site is terminated by the re uptake of norepinephrine by the neuron from which it was originally released.

Tricyclic Antidepressants

The tricyclic antidepressants are the most effective drugs presently available for the treatment of depression. These act by increasing the release of norepinephrine. Amphetamine and cocaine can also act in this manner. Imipramine, amitriptylin, and other closely related drugs are among the drugs currently most widely used for the treatment of major depression.

- imipramine (Tofranil)
- desipramine (Norpramin)



The activity of the tricyclic drugs depends on the central ring of seven or eight atoms which confers an angled or twisted conformation. The side chain must have at least 2 carbons although 3 appear to be better. The amine group may be either tertiary or secondary. All tricyclic antidepressants block the re-uptake of norepinephrine at nerve terminals. However, the potency and selectivity for the inhibition of the uptake of norepinephrine, serotonin, and dopamine vary greatly among the agents. The tertiary amine tricyclics seem to inhibit the serotonin uptake pump, whereas the secondary amine ones seem better in switching off the NE pump. For instance, imipramine is a potent and selective blocker of serotonin transport, while desipramine inhibits the uptake of norepinephrine.

Serotonin

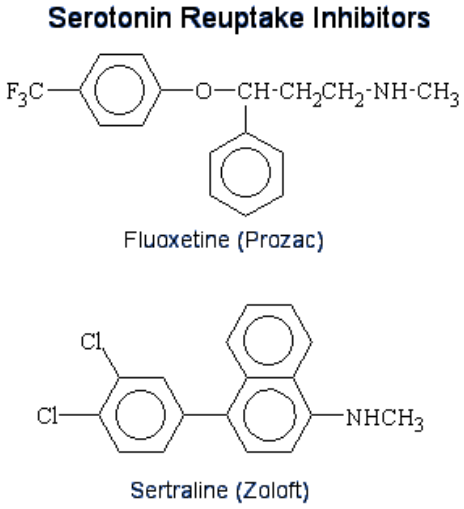
Serotonin (5-hydroxytryptamine or 5-HT) is a monoamine neurotransmitter found in cardiovascular tissue, in endothelial cells, in blood cells, and in the central nervous system. The role of serotonin in neurological function is diverse, and there is little doubt

that serotonin is an important CNS neurotransmitter. Although some of the serotonin is metabolized by monoamine oxidase, most of the serotonin released into the post-synaptic space is removed by the neuron through a re-uptake mechanism inhibited by the tricyclic antidepressants and the newer, more selective antidepressant re uptake inhibitors such as fluoxetine and sertraline.



Selective Serotonin Reuptake Inhibitors

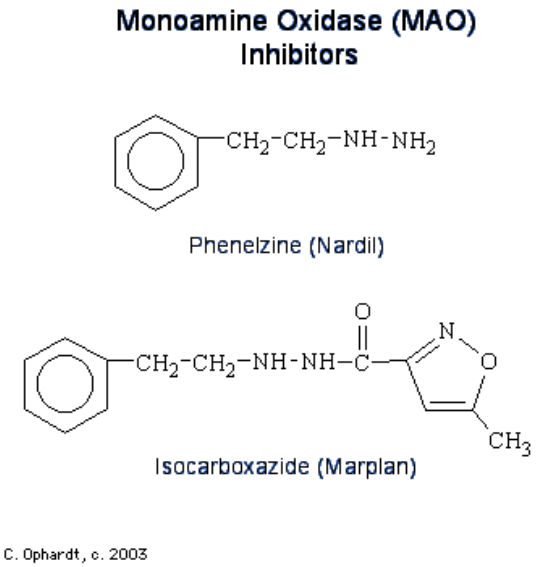
In recent years, selective serotonin reuptake inhibitors have been introduced for the treatment of depression. Prozac is the most famous drug in this class. Clomiprimine, fluoxetine (Prozac), sertraline and paroxetine selectively block the re uptake of serotonin, thereby increasing the levels of serotonin in the central nervous system. Note the similarities and differences between the tricyclic antidepressants and the selective serotonin re uptake inhibitors. Clomipramine has been useful in the treatment of obsessive-compulsive disorders.



Monoamine Oxidase Inhibitors

Monoamine oxidase (MAO) causes the oxidative deamination of norephinephrine, serotonin, and other amines. This oxidation is the method of reducing the concentration of the neurotransmitter after it has sent the signal at the receptor site. A drug which inhibits this enzyme has the effect of **increasing the concentration of the norepinephrine which in turn causes a stimulation effect.** Most MAO inhibitors are hydrazine derivatives. Hydrazine is highly reactive and may form a strong covalent bond with MAO with consequent inhibition for up to 5 days.

These drugs are less effective and produce more side effects than the tricyclic antidepressants. For example, they lower blood pressure and were at one time used to treat hypertension. Their use in psychiatry has also become very limited as the tricyclic antidepressants have come to dominate the treatment of depression and allied conditions. Thus, MAOIs are used most often when tricyclic antidepressants give unsatisfactory results.



Phenelzine is the hydrazine analog of phenylethylamine, a substrate of MAO. This and several other MAOIs, such as isocarboxazide, are structurally related to amphetamine and were synthesized in an attempt to enhance central stimulant properties.

- phenelzine (Nardil)
- isocarboxazid (Marplan)

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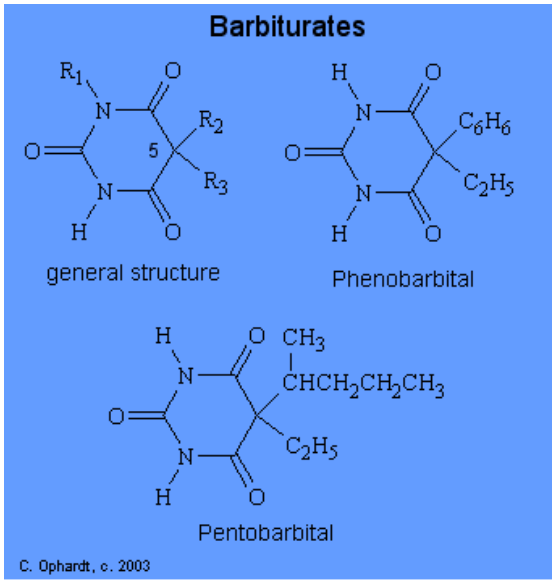
12.3.4: Barbiturates and Benzodiazepines

Hypnotic and sedative drugs are non-selective, general depressants of the central nervous system. If the dose is relatively low, a sedative action results in a reduction in restlessness and emotional tension. A larger dose of the same drug produces a hypnotic sleep inducing effect. As the dosage is increased further, the result is anesthesia or death if the dosage is sufficiently high.

Introduction

The barbiturates once enjoyed a long period of extensive use as sedative-hypnotic drugs; however, except for a few specialized uses, they have been largely replaced by the much safer benzodiazepines. Barbiturates are central nervous system depressants and are similar, in many ways, to the depressant effects of alcohol. To date, there are about 2,500 derivatives of barbituric acid of which only 15 are used medically. The first barbiturate was synthesized from barbituric acid in 1864. The original use of barbiturates was to replace drugs such as opiates, bromides, and alcohol to induce sleep.

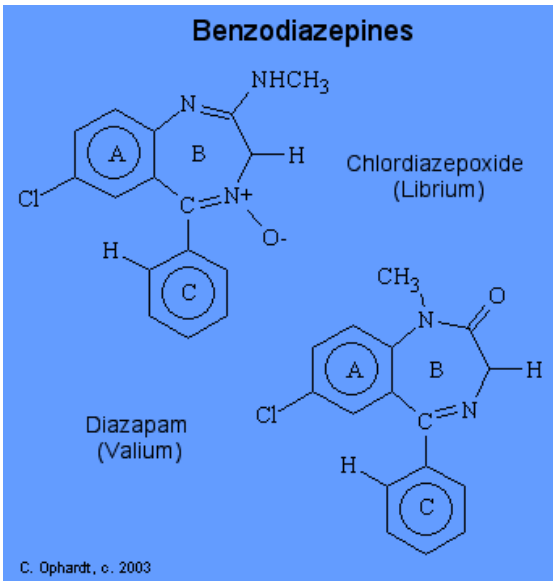
The hyponotic and sedative effects produced by barbiturates are usually ascribed to their interference of nerve transmission to the cortex. Various theories for the action of barbiturates include: changes in ion movements across the cell membrane; interactions with cholinergic and non cholinergic receptor sites; impairment of biochemical reactions which provide energy; and depression of selected areas of the brain. The structures of the barbiturates can be related to the duration of effective action. Although over 2000 derivatives of barbituric acid have been synthesized only about a dozen are currently used. All of the barbiturates are related to the structure of barbituric acid shown below.



The duration of effect depends mainly on the alkyl groups attached to carbon # 5 which confer lipid solubility to the drug. The duration of effective action decreases as the total number of carbons at C # 5 increases. To be more specific, a long effect is achieved by a short chain and/or phenyl group. A short duration effect occurs when there are the most carbons and branches in the alkyl chains

Benzodiazepines

The term benzodiazepine refers to the portion of the structure composed of a benzene ring (A) fused to a seven-membered diazepine ring (B). However, since all of the important benzodiazepines contain a aryl substituent ring C) and a 1, 4-diazepine ring, the term has come to mean the aryl-1,4-benzodiazepines. There are several useful benzodiazepines available: chlordiazepoxide (Librium) and diazapam (Valium).



The actions of benzodiazepines are a result of increased activation of receptors by gamma-aminobutyric acid (GABA). Benzodiazepine receptors are located on the alpha subunit of the GABA receptor located almost exclusively on postsynaptic nerve endings in the CNS (especially cerebral cortex). Benzodiazepines enhance the GABA transmitter in the opening of postsynaptic chloride channels which leads to hyperpolarization of cell membranes. That is, they "bend" the receptor slightly so that GABA molecules attach to and activate their receptors more effectively and more often.

Contributors

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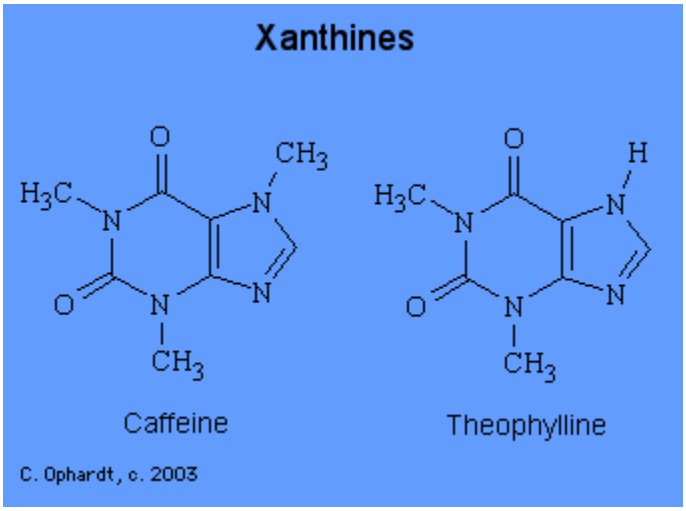
12.3.5: Drugs Acting Upon the Central Nervous System

The central nervous system directs the functions of all tissues of the body. The peripheral nervous system receives thousands of sensory inputs and transmits them to the brain via the spinal cord. The brain processes this incoming information and discards 99% as unimportant. After sensory information has been evaluated, selected areas of the central nervous system initiate nerve impulses to organs or tissue to make an appropriate response.

Chemical influences are capable of producing a myriad of effects on the activity and function of the central nervous system. Since our knowledge of different regions of brain function and the neurotransmitters in the brain is limited, the explanations for the mechanisms of drug action may be vague. The known neurotransmitters are: acetylcholine which is involved with memory and learning; *norepinephrine* which is involved with mania-depression and emotions; and *serotonin* which is involved with biological rhythms, sleep, emotion, and pain.

Central Nervous System Stimulants

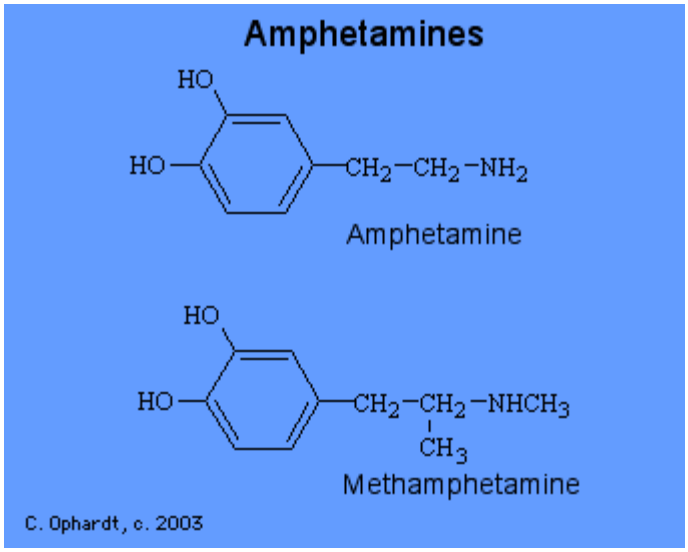
Stimulants are drugs that exert their action through excitation of the central nervous system. Psychic stimulants include caffeine, cocaine, and various amphetamines. These drugs are used to enhance mental alertness and reduce drowsiness and fatigue. However, increasing the dosage of caffeine above 200 mg (about 2 cups of coffee) does not increase mental performance but may increase nervousness, irritability, tremors, and headache. Heavy coffee drinkers become psychically dependent upon caffeine. If caffeine is withheld, a person may experience mild withdrawal symptoms characterized by irritability, nervousness, and headache.

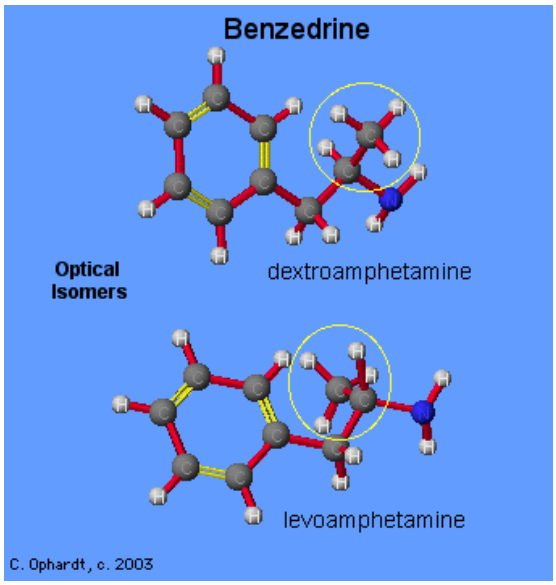


Caffeine and the chemically related xanthines, theophylline and theobromine, decrease in the order given in their stimulatory action. They may be included in some over-the-counter drugs. The action of caffeine is to block adenosine receptors as an antagonist. As caffeine has a similar structure to the adenosine group. This means that caffeine will fit adenosine receptors as well as adenosine itself. It inhibits the release of neurotransmitters from presynaptic sites but works in concert with norepinephrine or angiotensin to augment their actions. Antagonism of adenosine receptors by caffeine would appear to promote neurotransmitter release, thus explaining the stimulatory effects of caffeine.

Amphetamines

The stimulation caused by amphetamines is caused by excessive release of norepinephrine from storage sites in the peripheral nervous system. It is not known whether the same action occurs in the central nervous system. Two other theories for their action are that they are degraded slower than norepinephrine or that they could act on serotonin receptor sites. Therapeutic doses of amphetamine elevate mood, reduce feelings of fatigue and hunger, facilitate powers of concentration, and increase the desire and capacity to carry out work. They induce exhilarating feelings of power, strength, energy, self-assertion, focus and enhanced motivation. The need to sleep or eat is diminished.





Levoamphetamine (Benzedrine), dextroamphetamine (Dexedrine), and methamphetamine (Methedrine) are collectively referred to as amphetamines. Benzedrine is a mixture of both the dextro and levoamphetamine isomers. The dextro isomer is several times more potent than the levo isomer.

The misuse and abuse of amphetamines is a significant problem which may include the house wife taking diet pills, athletes desiring an improved performance, the truck driver driving non-stop coast to-coast, or a student cramming all night for an exam.

Contributors

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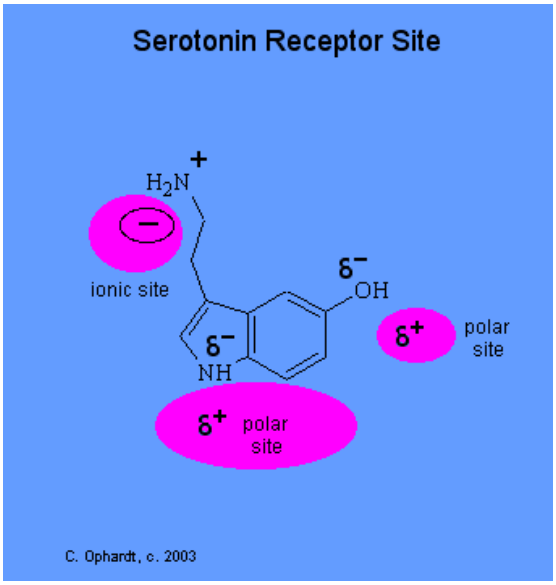
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12.3.6: Hallucinogenic Drugs

Hallucinogenic agents, also called psychomimetic agents, are capable of producing hallucinations, sensory illusions and bizarre thoughts. The primary effect of these compounds is to consistently alter thought and sensory perceptions. Some of these drugs are used in medicine to produce model psychoses as aids in psychotherapy. Another purpose is to investigate the relationship of mind, brain, and biochemistry with the purpose of elucidating mental diseases such as schizophrenia.

Introduction

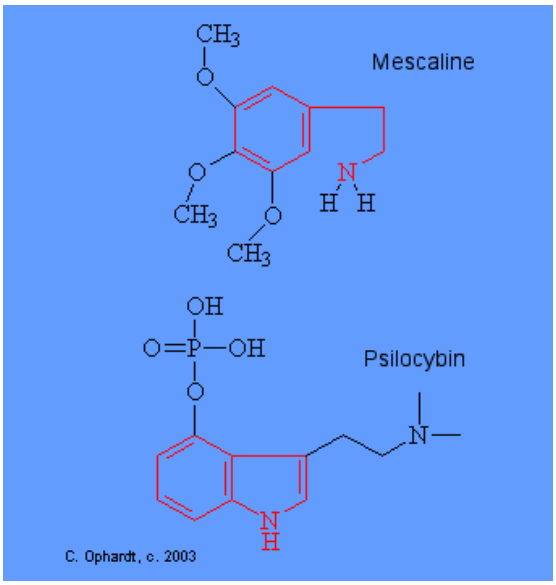
A large body of evidence links the action of hallucinogenic agents to effects at serotonin receptor sites in the central nervous system. Whether the receptor site is stimulated or blocked is not exactly known. The serotonin receptor site may consist of three polar or ionic areas to complement the structure of serotonin as shown in the graphic on the left.



Mescalin and Psilocybin

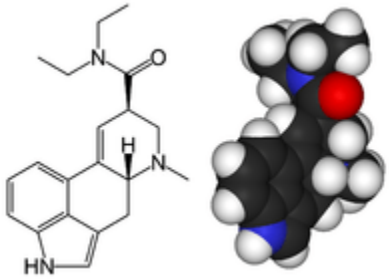
The drugs shown in the graphic can be isolated from natural sources: lysergic acid amide from morning glory seeds, psilocybin from the "magic mushroom", Psilocybe mexicana. The hallucinogenic molecules fit into the same receptors as the neuro-transmitter, and over-stimulate them, leading to false signals being created.

Mescaline is isolated from a peyote cactus. The natives of Central America first made use of these drugs in religious ceremonies, believing the vivid, colorful hallucinations had religious significance. The Aztecs even had professional mystics and prophets who achieved their inspiration by eating the mescaline-containing peyote cactus (Lophophora williamsii). Indeed, the cactus was so important to the Aztecs that they named it teo-nancacyl, or "God's Flesh". This plant was said to have been distributed to the guests at the coronation of Montezuma to make the ceremony seem even more spectacular.



Lysergic acid diethylamide (LSD)

LSD is one of the most powerful hallucinogenic drugs known. LSD stimulates centers of the sympathetic nervous system in the midbrain, which leads to pupillary dilation, increase in body temperature, and rise in the blood-sugar level. LSD also has a serotonin-blocking effect. The hallucinogenic effects of lysergic acid diethylamide (LSD) are also the result of the complex interactions of the drug with both the serotoninergic and dopaminergic systems.



During the first hour after ingestion, the user may experience visual changes with extreme changes in mood. The user may also suffer impaired depth and time perception, with distorted perception of the size and shape of objects, movements, color, sound, touch and the user's own body image.

Serotonin

Serotonin (5-hydroxytryptamine or 5-HT) is a monoamine neurotransmitter found in cardiovascular tissue, in endothelial cells, in blood cells, and in the central nervous system. The role of serotonin in neurological function is diverse, and there is little doubt that serotonin is an important CNS neurotransmitter. Although some of the serotonin is metabolized by monoamine oxidase, most of the serotonin released into the post-synaptic space is removed by the neuron through a re uptake mechanism inhibited by the tricyclic antidepressants and the newer, more selective antidepressant re uptake inhibitors such as fluoxetine and sertraline.



Outside Links

- en.Wikipedia.org/wiki/Lysergi...d_diethylamide
- en.Wikipedia.org/wiki/Serotonin

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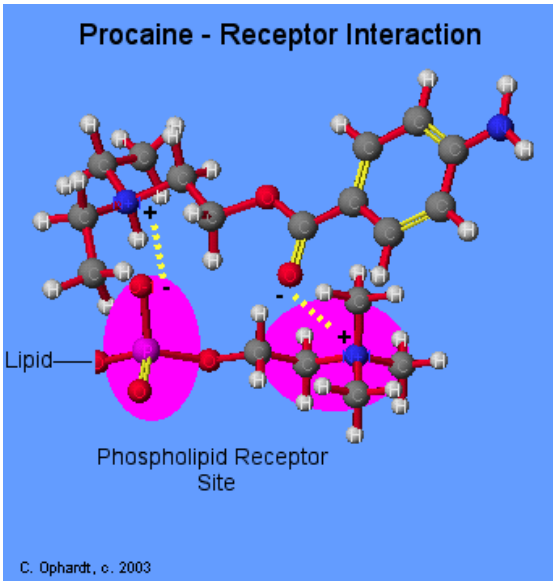
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12.3.7: Local Anesthetics

Unlike other drugs which act in the region of the synapse, local anesthetics are agents that reversibly block the generation and conduction of nerve impulses along a nerve fiber. They depress impulses from sensory nerves of the skin, surfaces of mucosa, and muscles to the central nervous system. These agents are widely used in surgery, dentistry, and ophthalmology to block transmission of impulses in peripheral nerve endings.

Introduction

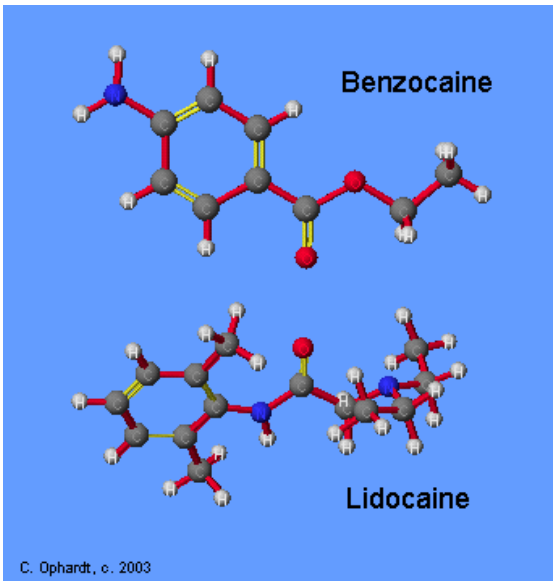
Most local anesthetics can be represented by the following general formula. In both the official chemical name and the proprietary name, a local anesthetic drug can be recognized by the "-caine" ending. The ester linkage can also be an amide linkage. The most recent research indicates that the local anesthetic binds to a phospholipid in the nerve membrane and inhibits the ability of the phospholipid to bind Ca^{+2} ions.



Practically all of the free-base forms of the drugs are liquids. For this reason most of these drugs are used as salts (chloride, sulfate, etc.) which are water soluble, odorless, and crystalline solids. As esters these drugs are easily hydrolyzed with consequent loss of activity. The amide form of the drug is more stable and resistant to hydrolysis.

Benzocaine and Lidocaine

Two local anesthtics are shown below.



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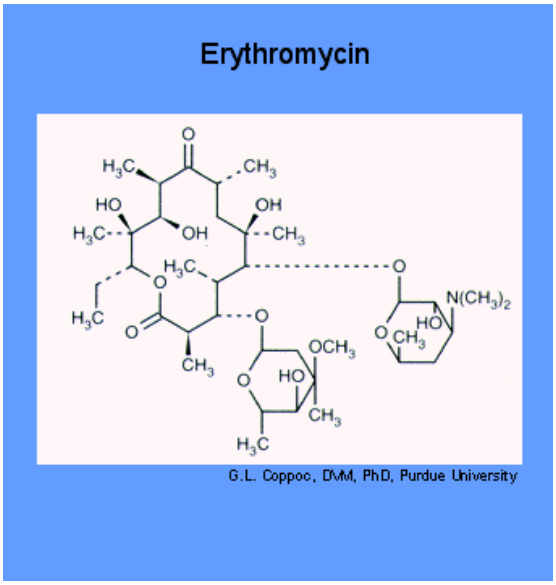
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12.3.8: Misc Antibiotics

Antibiotics are specific chemical substances derived from or produced by living organisms that are capable of inhibiting the life processes of other organisms. The first antibiotics were isolated from microorganisms but some are now obtained from higher plants and animals. Over 3,000 antibiotics have been identified but only a few dozen are used in medicine. Antibiotics are the most widely prescribed class of drugs comprising 12% of the prescriptions in the United States.

Macrolides

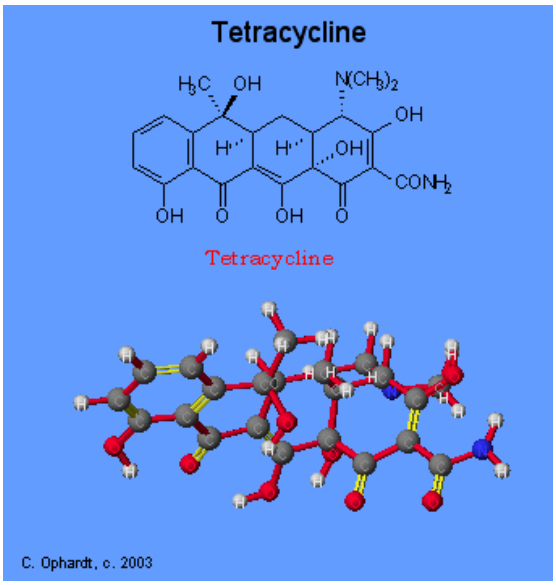
Macrolides are products of actinomycetes (soil bacteria) or semi-synthetic derivatives of them. Erythromycin is an orally effective antibiotic discovered in 1952 in the metabolic products of a strain of *Streptocyces erythreus*, originally obtained from a soil sample.



Erythromycin and other macrolide antibiotics inhibit protein synthesis by binding to the 23S rRNA molecule (in the 50S subunit) of the bacterial ribosome blocking the exit of the growing peptide chain. of sensitive microorganisms. (Humans do not have 50 S ribosomal subunits, but have ribosomes composed of 40 S and 60 S subunits). Certain resistant microorganisms with mutational changes in components of this subunit of the ribosome fail to bind the drug. The association between erythromycin and the ribosome is reversible and takes place only when the 50 S subunit is free from tRNA molecules bearing nascent peptide chains. Gram-positive bacteria accumulate about 100 times more erythromycin than do gram-negative microorganisms. The non ionized from of the drug is considerably more permeable to cells, and this probably explains the increased antimicrobial activity that is observed in alkaline pH.

Tetracyclines

Tetracyclines have the broadest spectrum of antimicrobial activity. These may include: Aureomycin, Terramycin, and Panmycin. Four fused 6-membered rings, as shown in the figure below, form the basic structure from which the various tetracyclines are made. The various derivatives are different at one or more of four sites on the rigid, planar ring structure. The classical tetracyclines were derived from *Streptomyces spp.*, but the newer derivatives are semisynthetic as is generally true for newer members of other drug groups.



Tetracyclines inhibit bacterial protein synthesis by blocking the attachment of the transfer RNA-amino acid to the ribosome. More precisely they are inhibitors of the codon-anticodon interaction. Tetracyclines can also inhibit protein synthesis in the host, but are less likely to reach the concentration required because eukaryotic cells do not have a tetracycline uptake mechanism.

Streptomycin

Streptomycin is effective against gram-negative bacteria, although it is also used in the treatment of tuberculosis. Streptomycin binds to the 30S ribosome and changes its shape so that it and inhibits protein synthesis by causing a misreading of messenger RNA information.

Chloramphenicol

Chloromycetin is also a broad spectrum antibiotic that possesses activity similar to the tetracylines. At present, it is the only antibiotic prepared synthetically. It is reserved for treatment of serious infections because it is potentially highly toxic to bone marrow cells. It inhibits protein synthesis by attaching to the ribosome and interferes with the formation of peptide bonds between amino acids. It behaves as an antimetabolite for the essential amino acid phenylalanine at ribosomal binding sites.

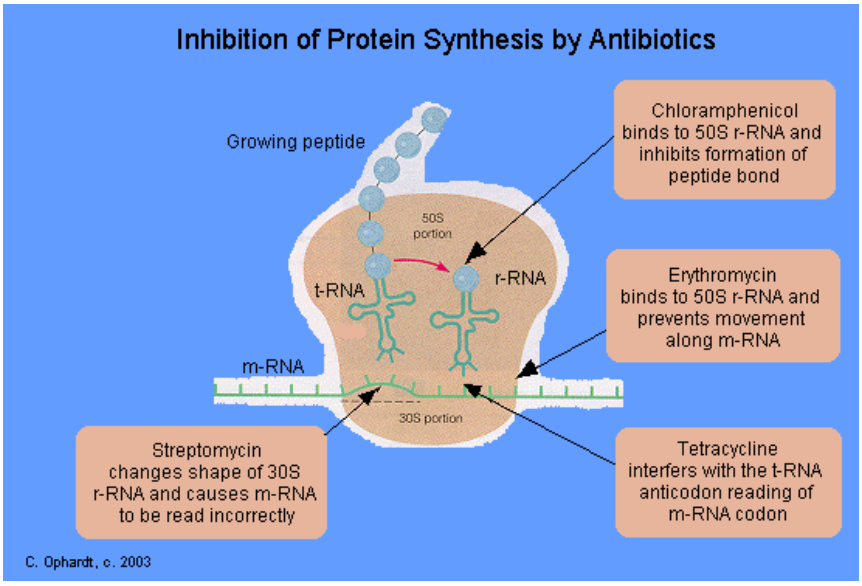


Table 1: Some clinically important antibiotics

Antibiotic	Producer organism	Activity	Site or mode of action
Penicillin	*Penicillium chrysogenum*	Gram-positive bacteria	Wall synthesis
Cephalosporin	*Cephalosporium acremonium*	Broad spectrum	Wall synthesis
Griseofulvin	*Penicillium griseofulvum*	Dermatophytic fungi	Microtubules
Bacitracin	*Bacillus subtilis*	Gram-positive bacteria	Wall synthesis
Polymyxin B	*Bacillus polymyxa*	Gram-negative bacteria	Cell membrane
Amphotericin B	*Streptomyces nodosus*	Fungi	Cell membrane
Erythromycin	*Streptomyces erythreus*	Gram-positive bacteria	Protein synthesis
Neomycin	*Streptomyces fradiae*	Broad spectrum	Protein synthesis
Streptomycin	*Streptomyces griseus*	Gram-negative bacteria	Protein synthesis
Tetracycline	*Streptomyces rimosus*	Broad spectrum	Protein synthesis
Vancomycin	*Streptomyces orientalis*	Gram-positive bacteria	Protein synthesis
Gentamicin	*Micromonospora purpurea*	Broad spectrum	Protein synthesis
Rifamycin	*Streptomyces mediterranei*	Tuberculosis	Protein synthesis

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12.3.9: Narcotic Analgesic Drugs

Narcotic agents are potent analgesics which are effective for the relief of severe pain. Analgesics are selective central nervous system depressants used to relieve pain. The term analgesic means "without pain". Even in therapeutic doses, narcotic analgesics can cause respiratory depression, nausea, and drowsiness. Long term administration produces tolerance, psychic, and physical dependence called addiction.

Introduction

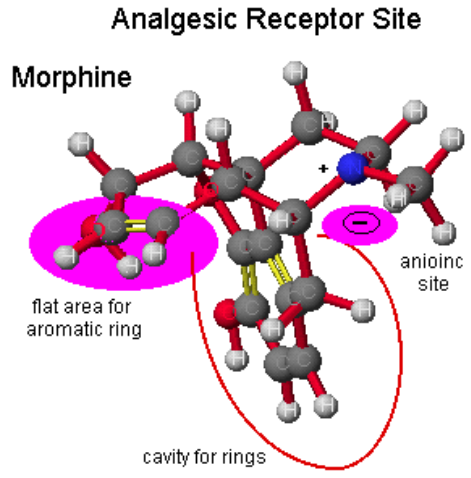
Narcotic agents may be classified into four categories:

1. Morphine and codeine - natural alkaloids of opium.
2. Synthetic derivatives of morphine such as heroin.
3. Synthetic agents which resemble the morphine structure.
4. Narcotic antagonists which are used as antidotes for overdoses of narcotic analgesics.

The main pharmacological action of analgesics is on the cerebrum and medulla of the central nervous system. Another effect is on the smooth muscle and glandular secretions of the respiratory and gastro-intestinal tract. The precise mechanism of action is unknown although the narcotics appear to interact with specific receptor sites to interfere with pain impulses.

Receptor Site

A schematic for an analgesic receptor site may look as shown in the graphic below with morphine. Three areas are needed: a flat areas to accommodate a flat nonpolar aromatic ring, a cavity to accept another series of rings perpendicular, and an anionic site for polar interaction of the amine group.



C. Ophardt, c. 2003

Enkephalins

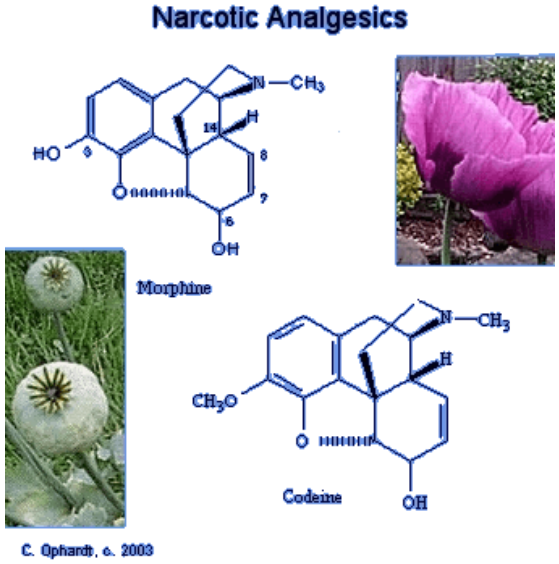
Recently investigators have discovered two compounds in the brain called enkephalins which resemble morphine in structure. Each one is a peptide composed of 5 amino acids and differ only in the last amino acid. The peptide sequences are: tyr-gly-gly-phe-leu and tyr-gly-gly-phe-met. Molecular models show that the structures of the enkephalins has some similarities with morphine. The main feature in common appears to be the aromatic ring with the -OH group attached (tyr). Methadone and other similar analgesics have 2 aromatic rings which would be similar to the enkephalins (tyr and phe).

Analgesics may relieve pain by preventing the release of acetylcholine. Enkephalin molecules are released from a nerve cell and bind to analgesic receptor sites on the nerve cell sending the impulse. The binding of enkephalin or morphine-like drugs changes the shape of the nerve sending the impulse in such a fashion as to prevent the cell from releasing acetylcholine. As a result, the pain impulse cannot be transmitted and the brain does not preceive pain.

Morphine and Codeine

Morphine exerts a narcotic action manifested by analgesia, drowsiness, changes in mood, and mental clouding. The major medical action of morphine sought in the CNS is analgesia. Opiates suppress the "cough center" which is also located in the brain stem, the medulla. Such an action is thought to underlie the use of opiate narcotics as cough suppressants. Codeine appears to be particularly effective in this action and is widely used for this purpose.

Narcotic analgesics cause an addictive physical dependence. If the drug is discontinued, withdrawal symptoms are experienced. Although the reasons for addiction and withdrawal symptoms are not completely known, recent experiments have provided some information. A nucleotide known as cyclicadenosine monophosphate (cAMP) is synthesized with the aid of the enzyme adenylate cyclase. Enkephalin and morphine-like drugs inhibit this enzyme and thus decrease the amount of cAMP in the cells. In order to compensate for the decreased cAMP, the cells synthesize more enzyme in an attempt to produce more cAMP. Since more enzyme has been produced, more morphine is required as an inhibitor to keep the cAMP at a low level. This cycle repeats itself causing an increase in the tolerance level and increasing the amounts of morphine required. If morphine is suddenly withheld, withdrawal symptoms are probably caused by a high concentration of cAMP since the synthesizing enzyme, adenylate cyclase, is no longer being inhibited.



Morphine and codeine are contained in opium from the poppy (*Papaver Somniterum*) plant found in Turkey, Mexico, Southeast Asia, China, and India. This plant is 3-4 feet tall with 5-8 egg shaped capsules on top. Ten days after the poppy blooms in June, incisions are made in the capsules permitting a milky fluid to ooze out. The following day the gummy mass (now brown) is carefully scraped off and pressed into cakes of raw opium to dry.

Opium contains over 20 compounds but only morphine (10%) and codeine (0.5%) are of any importance. Morphine is extracted from the opium and isolated in a relatively pure form. Since codeine is in such low concentration, it is synthesized from morphine by an ether-type methylation of an alcohol group. Codeine has only a fraction of the potency compared to morphine. It is used with aspirin and as a cough suppressant.

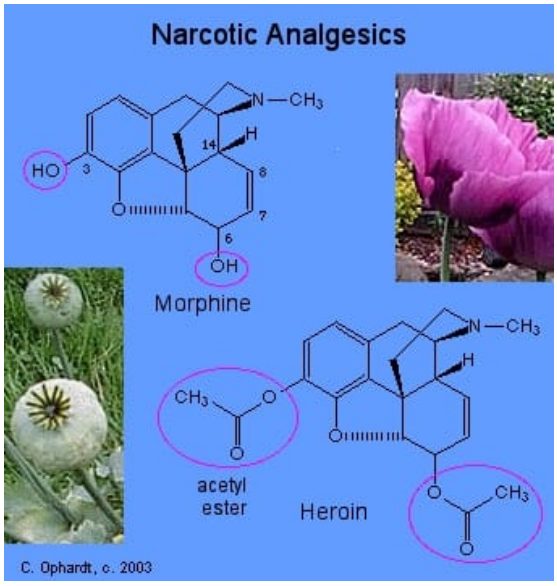
Heroin

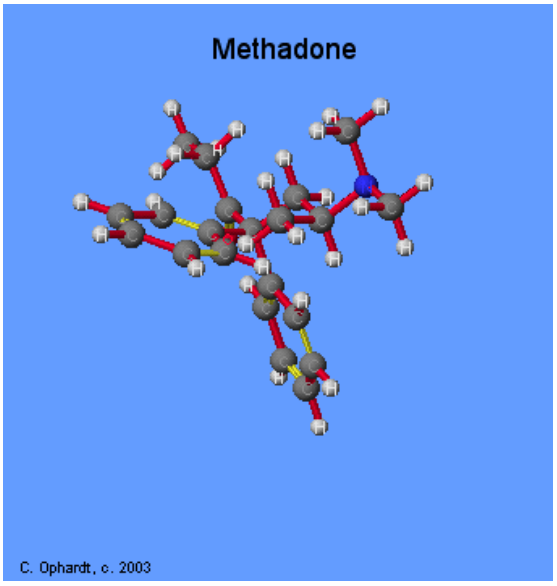
Heroin is synthesized from morphine by a relatively simple esterification reaction of two alcohol (phenol) groups with acetic anhydride (equivalent to acetic acid). Heroin is much more potent than morphine but without the respiratory depression effect. A possible reason may be that heroin passes the blood-brain barrier much more rapidly than morphine. Once in the brain, the

heroin is hydrolyzed to morphine which is responsible for its activity.

Synthetic narcotic analgesics include meperidine and methadone. Meperidine is the most common subsitute for morphine. It exerts several pharmacological effects: analgesic, local anesthetic, and mild antihistamine. This multiple activity may be explained by its structural resemblance to morphine, atropine, and histamine.

Methadone is more active and more toxic than morphine. It can be used for the relief of may types of pain. In addition it is used as a narcotic substitute in addiction treatment because it prevents morphine abstinence syndrome. Methadone was synthesized by German chemists during Wold War II when the United States and our allies cut off their opium supply. And it is difficult to fight a war without analgesics so the Germans went to work and synthesized a number of medications in use today, including demerol and darvon which is structurally simular to methadone. And before we go further lets clear up another myth. Methadone, or dolophine was not named after Adolf Hitler. The "dol" in dolophine comes from the latin root "dolor." The female name Dolores is derived from it and the term dol is used in pain research to measure pain e.g., one dol is 1 unit of pain.

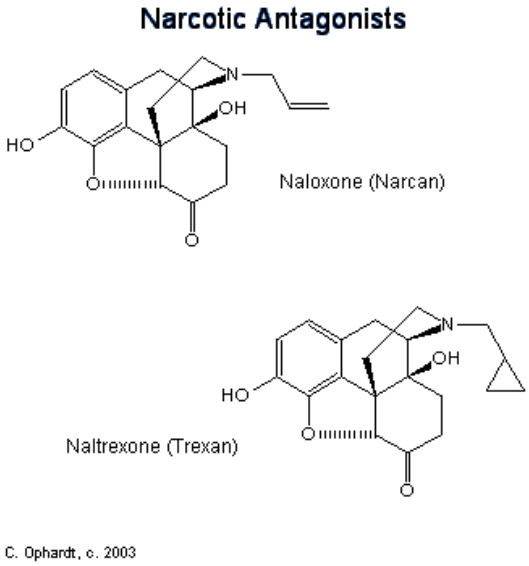




Even methadone, which looks strikingly different from other opioid agonists, has steric forces which produce a configuration that closely resembles that of other opiates. See the graphic on the left and the top graphic on this page. In other words, steric forces bend the molecule of methadone into the correct configuration to fit into the opiate receptor. When you take methadone it first must be metabolized in the liver to a product that your body can use. Excess methadone is also stored in the liver and blood stream and this is how methadone works its 'time release trick' and last for 24 hours or more. Once in the blood stream metabolized methadone is slowly passed to the brain when it is needed to fill opiate receptors. Methadone is the only effective treatment for heroin addiction. It works to smooth the ups and down of heroin craving and allows the person to function normally.

Narcotic Antagonists

Narcotic Antagonists prevent or abolish excessive respiratory depression caused by the administration of morphine or related compounds. They act by competing for the same analgesic receptor sites. They are structurally related to morphine with the exception of the group attached to nitrogen.



Nalorphine precipitates withdrawal symptoms and produces behavioral disturbances in addition to the antogonism action. Naloxane is a pure antagonist with no morphine like effects. It blocks the euphoric effect of heroin when given before heroin. Naltrexone became clinically available in 1985 as a new narcotic antagonist. Its actions resemble those of naloxone, but naltrexone is well is well absorbed orally and is long acting, necessitating only a dose of 50 to 100 mg. Therefore, it is useful in narcotic treatment programs where it is desired to maintain an individual on chronic therapy with a narcotic antagonist. In individuals taking naltrexone, subsequent injection of an opiate will produce little or no effect. Naltrexone appears to be particularly effective for the treatment of narcotic dependence in addicts who have more to gain by being drug-free rather than drug dependant

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12.3.10: Penicillin

The penicillins were the first antibiotics discovered as natural products from the mold Penicillium.

Introduction

In 1928, Sir Alexander Fleming, professor of bacteriology at St. Mary's Hospital in London, was culturing *Staphylococcus aureus*. He noticed zones of inhibition where mold spores were growing. He named the mold Penicillium rubrum. It was determined that a secretion of the mold was effective against Gram-positive bacteria.

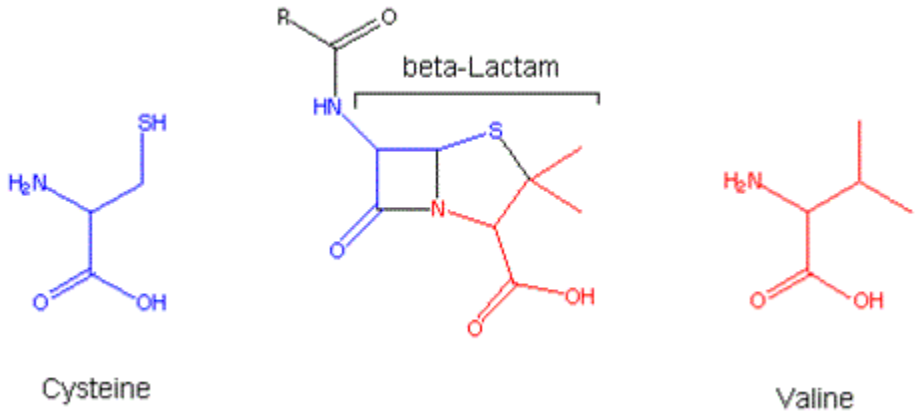


Figure 1: Beta Lactam Structure

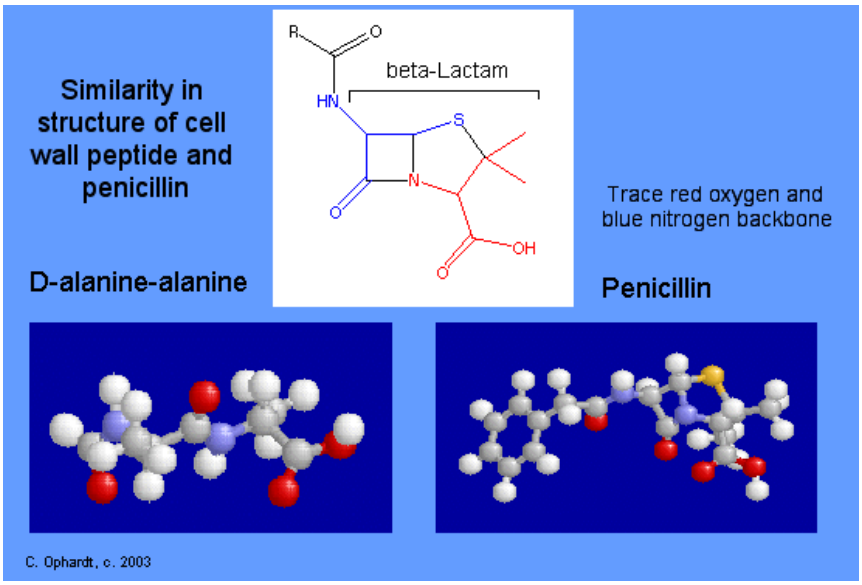
Penicillins as well as cephalosporins are called beta-lactam antibiotics and are characterized by three fundamental structural requirements: the fused beta-lactam structure (shown in the blue and red rings, a free carboxyl acid group (shown in red bottom right), and one or more substituted amino acid side chains (shown in black). The lactam structure can also be viewed as the covalent bonding of pieces of two amino acids - cysteine (blue) and valine (red).

Penicillin-G where R = an ethyl pheny group, is the most potent of all penicillin derivatives. It has several shortcomings and is effective only against gram-positive bacteria. It may be broken down in the stomach by gastric acids and is poorly and irregularly absorbed into the blood stream. In addition many disease producing staphylococci are able to produce an enzyme capable of inactivating penicillin-G. Various semisynthetic derivatives have been produced which overcome these shortcomings.

Powerful electron-attracting groups attached to the amino acid side chain such as in phenethicillin prevent acid attack. A bulky group attached to the amino acid side chain provides steric hindrance which interferes with the enzyme attachment which would deactivate the pencillins i.e. methicillin. Refer to Table 2 for the structures. Finally if the polar character is increased as in ampicillin or carbenicillin, there is a greater activity against Gram-negative bacteria.

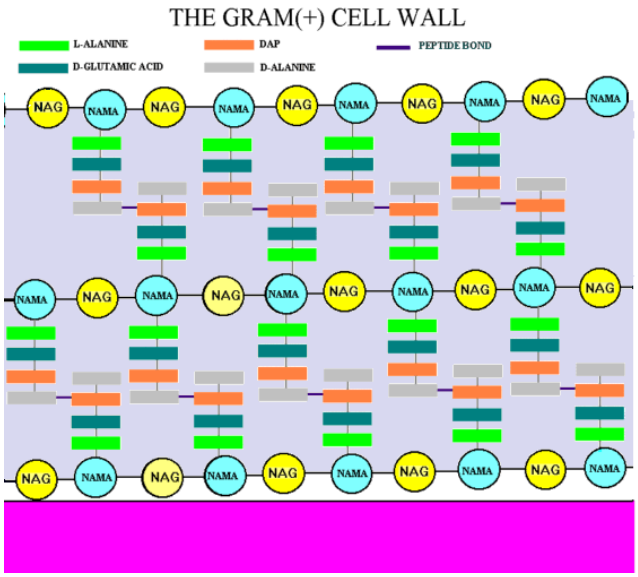
Penicillin Mode of Action

All penicillin derivatives produce their bacteriocidal effects by inhibition of bacterial cell wall synthesis. Specifically, the cross linking of peptides on the mucosaccharide chains is prevented. If cell walls are improperly made cell walls allow water to flow into the cell causing it to burst. Resemblances between a segment of penicillin structure and the backbone of a peptide chain have been used to explain the mechanism of action of beta-lactam antibiotics. The structures of a beta-lactam antibiotic and a peptide are shown on the left for comparison. Follow the trace of the red oxygens and blue nitrogen atoms.



Gram-positive bacteria possess a thick cell wall composed of a cellulose-like structural sugar polymer covalently bound to short peptide units in layers.The polysaccharide portion of the peptidoglycan structure is made of repeating units of N-acetylglucosamine linked b-1,4 to N-acetylmuramic acid (NAG-NAM). The peptide varies, but begins with L-Ala and ends with D-Ala. In the middle is a dibasic amino acid, diaminopimelate (DAP). DAP (orange) provides a linkage to the D-Ala (gray) residue on an adjacent peptide.

The bacterial cell wall synthesis is completed when a cross link between two peptide chains attached to polysaccharide backbones is formed. The cross linking is catalyzed by the enzyme transpeptidase. First the terminal alanine from each peptide is hydrolyzed and secondly one alanine is joined to lysine through an amide bond.



Peptidoglycan image courtesy of the University of Texas-Houston Medical School

Penicillin binds at the active site of the transpeptidase enzyme that cross-links the peptidoglycan strands. It does this by mimicking the D-alanyl-D-alanine residues that would normally bind to this site. Penicillin irreversibly inhibits the enzyme transpeptidase by reacting with a serine residue in the transpeptidase. This reaction is irreversible and so the growth of the bacterial cell wall is inhibited. Since mammal cells do not have the same type of cell walls, penicillin specifically inhibits only bacterial cell wall synthesis.

Bacterial Resistance

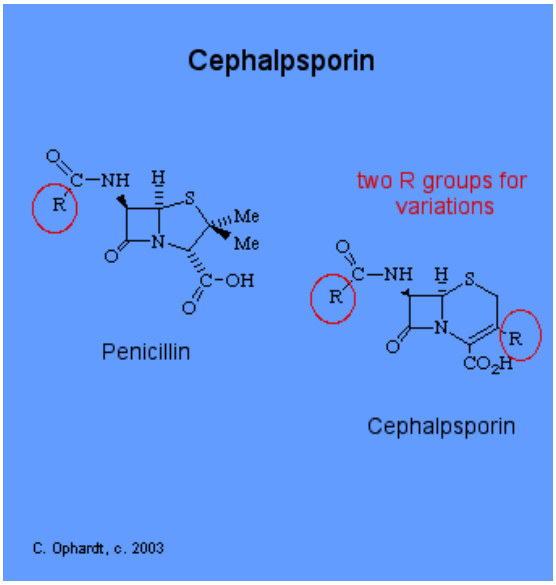
As early as the 1940s, bacteria began to combat the effectiveness of penicillin. Penicillinases (or beta-lactamases) are enzymes produced by structurally susceptable bacteria which renders penicillin useless by hydrolysing the peptide bond in the beta-lactam ring of the nucleus. Penicillinase is a response of bacterial adaptation to its adverse environment, namely the presence of a substance which inhibits its growth. Many other antibiotics are also rendered ineffective because of this same type of resistance.

Severe Allergic Shock

It is estimated that between 300-500 people die each year from penicillin-induced anaphylaxis, a severe allergic shock reaction to penicillin. In afflicted individuals, the beta-lactam ring binds to serum proteins, initiating an IgE-mediated inflammatory response. Penicillin and ala-ala peptide - Chime in new window

Cephalosporins

Cephalosporins are the second major group of beta-lactam antibiotics. They differ from penicillins by having the beta-lactam ring as a 6 member ring. The other difference, which is more significant from a medicinal chemistry stand point, is the existence of a functional group (R) at position 3 of the fused ring system. This now allows for molecular variations to effect changes in properties by diversifying the groups at position 3.



The first member of the newer series of beta-lactams was isolated in 1956 from extracts of Cephalosporium acremonium, a sewer fungus. Like penicillin, cephalosporins are valuable because of their low toxicity and their broad spectrum of action against various diseases. In this way, cephalosporin is very similar to penicillin. Cephalosporins are one of the most widely used antibiotics, and economically speaking, has about 29% of the antibiotic market. The cephalosporins are possibly the single most important group of antibiotics today and are equal in importance to penicillin.

The structure and mode of action of the cephalosporins are similar to that of penicillin. They affect bacterial growth by inhibiting cell wall synthesis, in Gram-positive and negative bacteria. Some brand names include: cefachlor, cefadroxil, cefoxitin, ceftriaxone. Cephalexin

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12.3.11: Sulfa Drugs

Sulfonamides are synthetic antimicrobial agents with a wide spectrum encompassing most gram-positive and many gram-negative organisms. These drugs were the first efficient treatment to be employed systematically for the prevention and cure of bacterial infections.

Contributors and Attributions

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12.4: MATERIALS FOR ELECTRONICS

12.4.1: Bonding in Electronic Materials
12.4.2: Silicon Devices

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12.4.1: Bonding in Electronic Materials

Bonding in metals and semiconductors can be described using band theory, in which a set of molecular orbitals is generated that extends throughout the solid. The primary learning objective of this Module is to describe the electrical properties of solid using band theory.

Band Theory

To explain the observed properties of metals, a more sophisticated approach is needed than the electron-sea model commonly described. The molecular orbital theory used to explain the delocalized π bonding in polyatomic ions and molecules such as NO_2^-, ozone, and 1,3-butadiene can be adapted to accommodate the much higher number of atomic orbitals that interact with one another simultaneously in metals.

In a 1 mol sample of a metal, there can be more than 10^{24} orbital interactions to consider. In our molecular orbital description of metals, however, we begin by considering a simple one-dimensional example: a linear arrangement of n metal atoms, each containing a single electron in an s orbital. We use this example to describe an approach to metallic bonding called band theory, which assumes that the valence orbitals of the atoms in a solid interact, generating a set of molecular orbitals that extend throughout the solid.

One-Dimensional Systems

If the distance between the metal atoms is short enough for the orbitals to interact, they produce bonding, antibonding, and nonbonding molecular orbitals. The left portion of Figure 12.4.1.1 shows the pattern of molecular orbitals that results from the interaction of ns orbitals as n increases from 2 to 5.

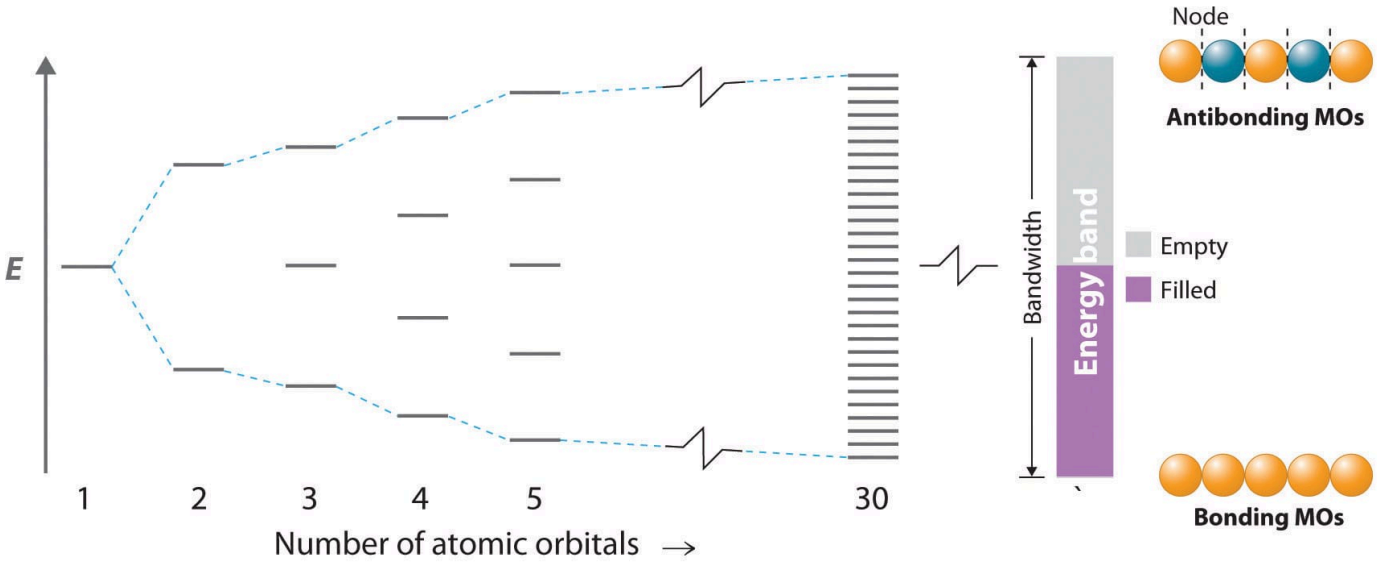


Figure 12.4.1.1: The Molecular Orbital Energy-Level Diagram for a Linear Arrangement of n Atoms, Each of Which Contains a Singly Occupied s Orbital. As n becomes very large, the energy separation between adjacent levels becomes so small that a single continuous band of allowed energy levels results. The lowest-energy molecular orbital corresponds to positive overlap between all the atomic orbitals to give a totally bonding combination, whereas the highest-energy molecular orbital contains a node between each pair of atoms and is thus totally antibonding.

As we saw previously, the lowest-energy orbital is the completely bonding molecular orbital, whereas the highest-energy orbital is the completely antibonding molecular orbital. Molecular orbitals of intermediate energy have fewer nodes than the totally antibonding molecular orbital. The energy separation between adjacent orbitals decreases as the number of interacting orbitals increases. For n = 30, there are still discrete, well-resolved energy levels, but as n increases from 30 to a number close

to Avogadro's number, the spacing between adjacent energy levels becomes almost infinitely small. The result is essentially a continuum of energy levels, as shown on the right in Figure 12.4.1.1, each of which corresponds to a particular molecular orbital extending throughout the linear array of metal atoms. The levels that are lowest in energy correspond to mostly bonding combinations of atomic orbitals, those highest in energy correspond to mostly antibonding combinations, and those in the middle correspond to essentially nonbonding combinations.

The continuous set of allowed energy levels shown on the right in Figure 12.4.1.1 is called an energy band. The difference in energy between the highest and lowest energy levels is the bandwidth and is proportional to the strength of the interaction between orbitals on adjacent atoms: the stronger the interaction, the larger the bandwidth. Because the band contains as many energy levels as molecular orbitals, and the number of molecular orbitals is the same as the number of interacting atomic orbitals, the band in Figure 12.4.1.1 contains n energy levels corresponding to the combining of s orbitals from n metal atoms. Each of the original s orbitals could contain a maximum of two electrons, so the band can accommodate a total of 2n electrons. Recall, however, that each of the metal atoms we started with contained only a single electron in each s orbital, so there are only n electrons to place in the band. Just as with atomic orbitals or molecular orbitals, the electrons occupy the lowest energy levels available. Consequently, only the lower half of the band is filled. This corresponds to filling all of the bonding molecular orbitals in the linear array of metal atoms and results in the strongest possible bonding.

Multidimensional Systems

The previous example was a one-dimensional array of atoms that had only s orbitals. To extrapolate to two- or three-dimensional systems and atoms with electrons in p and d orbitals is straightforward in principle, even though in practice the mathematics becomes more complex, and the resulting molecular orbitals are more difficult to visualize. The resulting energy-level diagrams are essentially the same as the diagram of the one-dimensional example in Figure 12.4.1.1, with the following exception: they contain as many bands as there are different types of interacting orbitals. Because different atomic orbitals interact differently, each band will have a different bandwidth and will be centered at a different energy, corresponding to the energy of the parent atomic orbital of an isolated atom.

Band Gap

Because the 1s, 2s, and 2p orbitals of a period 3 atom are filled core levels, they do not interact strongly with the corresponding orbitals on adjacent atoms. Hence they form rather narrow bands that are well separated in energy (Figure 12.4.1.2). These bands are completely filled (both the bonding and antibonding levels are completely populated), so they do not make a net contribution to bonding in the solid. The energy difference between the highest level of one band and the lowest level of the next is the band gap. It represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.

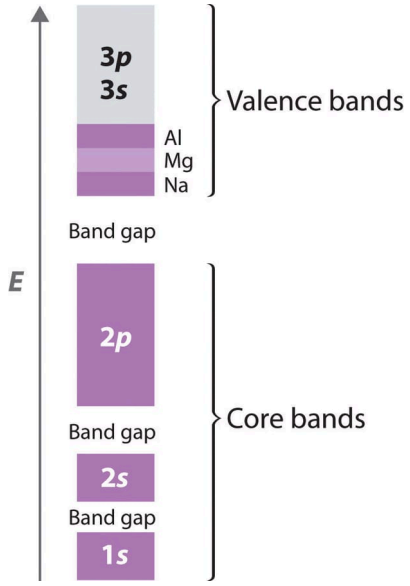


Figure 12.4.1.2: The Band Structures of the Period 3 Metals Na, Mg, and Al. The 3s and 3p valence bands overlap in energy to form a continuous set of energy levels that can hold a maximum of eight electrons per atom.

Because they extend farther from the nucleus, the valence orbitals of adjacent atoms (3s and 3p in Figure 12.4.1.2) interact much more strongly with one another than do the filled core levels; as a result, the valence bands have a larger bandwidth. In fact, the bands derived from the 3s and 3p atomic orbitals are wider than the energy gap between them, so the result is overlapping bands. These have molecular orbitals derived from two or more valence orbitals with similar energies. As the valence band is filled with one, two, or three electrons per atom for Na, Mg, and Al, respectively, the combined band that arises from the overlap of the 3s and 3p bands is also filling up; it has a total capacity of eight electrons per atom (two electrons for each 3s orbital and six electrons for each set of 3p orbitals). With Na, therefore, which has one valence electron, the combined valence band is one-eighth filled; with Mg (two valence electrons), it is one-fourth filled; and with Al, it is three-eighths filled, as indicated in Figure 12.4.1.2. The partially filled valence band is absolutely crucial for explaining metallic behavior because it guarantees that there are unoccupied energy levels at an infinitesimally small energy above the highest occupied level.

Band theory can explain virtually all the properties of metals. Metals conduct electricity, for example, because only a very small amount of energy is required to excite an electron from a filled level to an empty one, where it is free to migrate rapidly throughout the crystal in response to an applied electric field. Similarly, metals have high heat capacities (as you no doubt remember from the last time a doctor or a nurse placed a stethoscope on your skin) because the electrons in the valence band can absorb thermal energy by being excited to the low-lying empty energy levels. Finally, metals are lustrous because light of various wavelengths can be absorbed, causing the valence electrons to be excited into any of the empty energy levels above the highest occupied level. When the electrons decay back to low-lying empty levels, they emit light of different wavelengths. Because electrons can be excited from many different filled levels in a metallic solid and can then decay back to any of many empty levels, light of varying wavelengths is absorbed and reemitted, which results in the characteristic shiny appearance that we associate with metals.

Requirements for Metallic Behavior

For a solid to exhibit metallic behavior,

- it must have a set of delocalized orbitals forming a band of allowed energy levels, and
- the resulting band must be partially filled (10%–90%) with electrons.

Without a set of delocalized orbitals, there is no pathway by which electrons can move through the solid.

Band theory explains the correlation between the valence electron configuration of a metal and the strength of metallic bonding. The valence electrons of transition metals occupy either their valence ns, (n – 1)d, and np orbitals (with a total capacity of 18 electrons per metal atom) or their ns and (n – 1)d orbitals (a total capacity of 12 electrons per metal atom). These atomic orbitals are close enough in energy that the derived bands overlap, so the valence electrons are not confined to a specific orbital. Metals with 6 to 9 valence electrons (which correspond to groups 6–9) are those most likely to fill the valence bands approximately halfway. Those electrons therefore occupy the highest possible number of bonding levels, while the number of antibonding levels occupied is minimal. Not coincidentally, the elements of these groups exhibit physical properties consistent with the presence of the strongest metallic bonding, such as very high melting points.

Insulators

In contrast to metals, electrical insulators are materials that conduct electricity poorly because their valence bands are full. The energy gap between the highest filled levels and the lowest empty levels is so large that the empty levels are inaccessible: thermal energy cannot excite an electron from a filled level to an empty one. The valence-band structure of diamond, for example, is shown in Figure 12.4.1.3a. Because diamond has only 4 bonded neighbors rather than the 6 to 12 typical of metals, the carbon 2s and 2p orbitals combine to form two bands in the solid, with the one at lower energy representing bonding molecular orbitals and the one at higher energy representing antibonding molecular orbitals. Each band can accommodate four electrons per atom, so only the lower band is occupied. Because the energy gap between the filled band and the empty band is very large (530 kJ/mol), at normal temperatures thermal energy cannot excite electrons from the filled level into the empty band. Thus there is no pathway by which electrons can move through the solid, so diamond has one of the lowest electrical conductivities known.

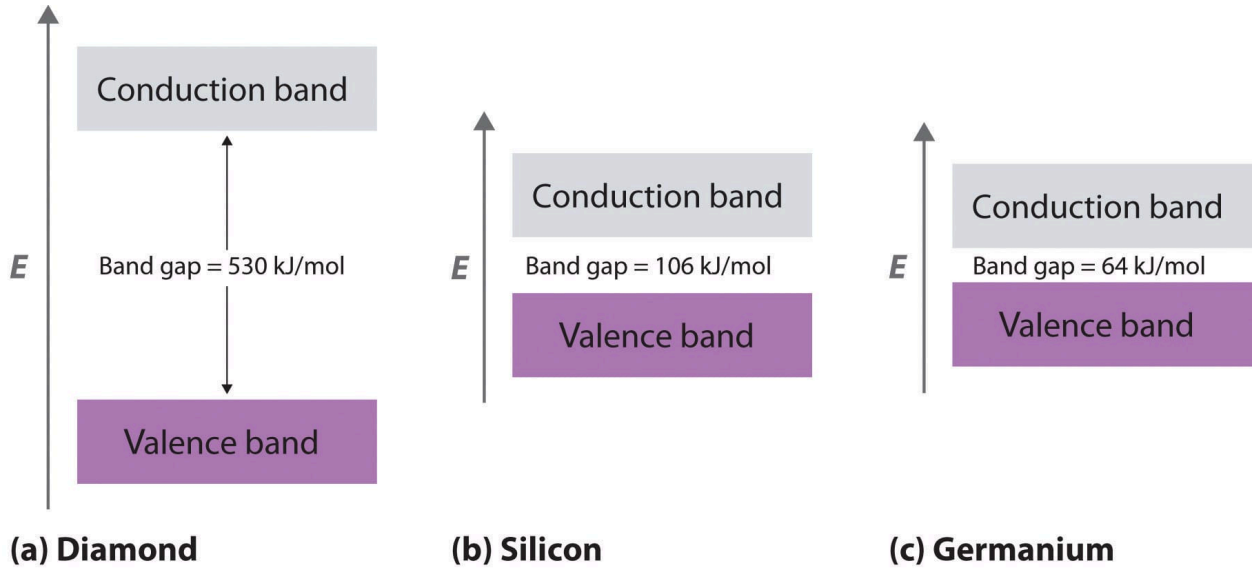


Figure 12.4.1.2: Energy-Band Diagrams for Diamond, Silicon, and Germanium. The band gap gets smaller from C to Ge.

Semiconductors

What if the difference in energy between the highest occupied level and the lowest empty level is intermediate between those of electrical conductors and insulators? This is the case for silicon and germanium, which have the same structure as diamond. Because Si–Si and Ge–Ge bonds are substantially weaker than C–C bonds, the energy gap between the filled and empty bands becomes much smaller as we go down group 14 (part (b) and part (c) of Figure 12.4.1.2). Consequently, thermal energy is able to excite a small number of electrons from the filled valence band of Si and Ge into the empty band above it, which is called the conduction band.

Exciting electrons from the filled valence band to the empty conduction band causes an increase in electrical conductivity for two reasons:

1. The electrons in the previously vacant conduction band are free to migrate through the crystal in response to an applied electric field.
2. Excitation of an electron from the valence band produces a “hole” in the valence band that is equivalent to a positive charge. The hole in the valence band can migrate through the crystal in the direction opposite that of the electron in the conduction band by means of a “bucket brigade” mechanism in which an adjacent electron fills the hole, thus generating a hole where the second electron had been, and so forth.

Consequently, Si is a much better electrical conductor than diamond, and Ge is even better, although both are still much poorer conductors than a typical metal (Figure 12.4.1.4).

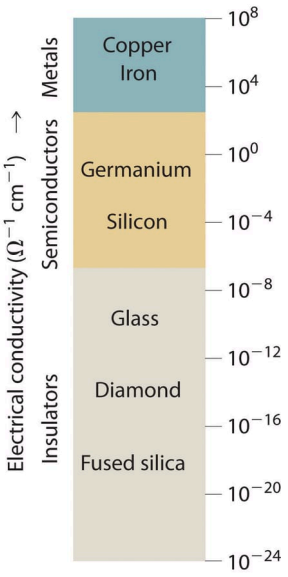


Figure 12.4.1.4: A Logarithmic Scale Illustrating the Enormous Range of Electrical Conductivities of Solids

Substances such as Si and Ge that have conductivities between those of metals and insulators are called semiconductors. Many binary compounds of the main group elements exhibit semiconducting behavior similar to that of Si and Ge. For example, gallium arsenide (GaAs) is isoelectronic with Ge and has the same crystalline structure, with alternating Ga and As atoms; not surprisingly, it is also a semiconductor. The electronic structure of semiconductors is compared with the structures of metals and insulators in Figure 12.4.1.5.

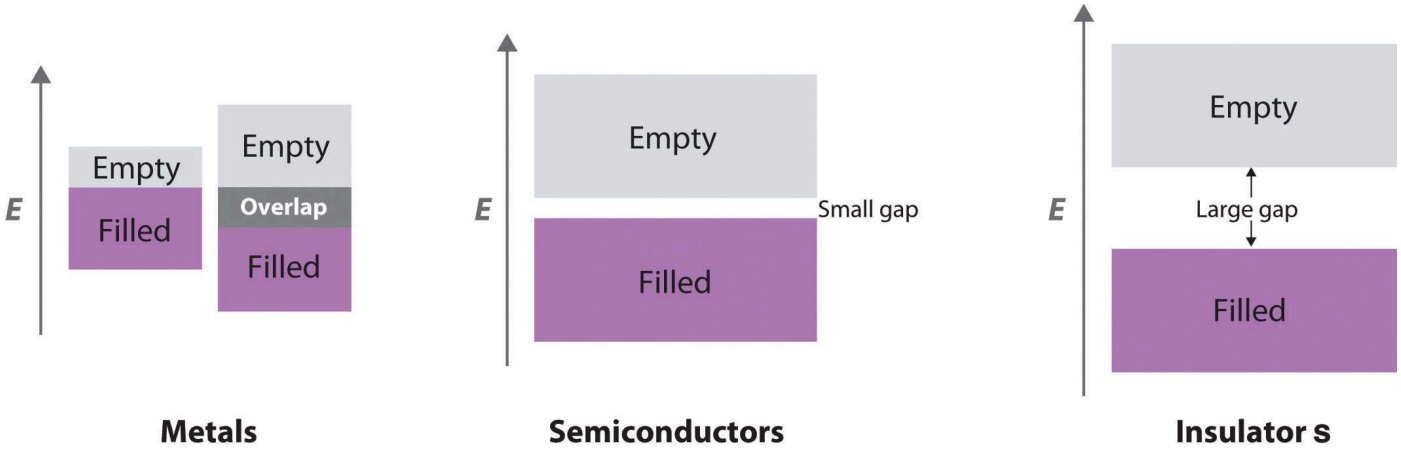


Figure 12.4.1.5: A Comparison of the Key Features of the Band Structures of Metals, Semiconductors, and Insulators. Metallic behavior can arise either from the presence of a single partially filled band or from two overlapping bands (one full and one empty).

Temperature and Conductivity

Because thermal energy can excite electrons across the band gap in a semiconductor, increasing the temperature increases the number of electrons that have sufficient kinetic energy to be promoted into the conduction band. The electrical conductivity of a semiconductor therefore increases rapidly with increasing temperature, in contrast to the behavior of a purely metallic crystal. In a metal, as an electron travels through the crystal in response to an applied electrical potential, it cannot travel very far before it encounters and collides with a metal nucleus. The more often such encounters occur, the slower the net motion of the electron through the crystal, and the lower the conductivity. As the temperature of the solid increases, the metal atoms in the lattice acquire more and more kinetic energy. Because their positions are fixed in the lattice, however, the increased kinetic energy increases only the extent to which they vibrate about their fixed positions. At higher temperatures, therefore, the metal nuclei collide with the mobile electrons more frequently and with greater energy, thus decreasing the conductivity. This effect is, however, substantially smaller than the increase in conductivity with temperature exhibited by semiconductors. For example, the conductivity of a tungsten wire decreases by a factor of only about two over the temperature range 750–1500 K, whereas the

conductivity of silicon increases approximately 100-fold over the same temperature range. These trends are illustrated in Figure 12.4.1.6.

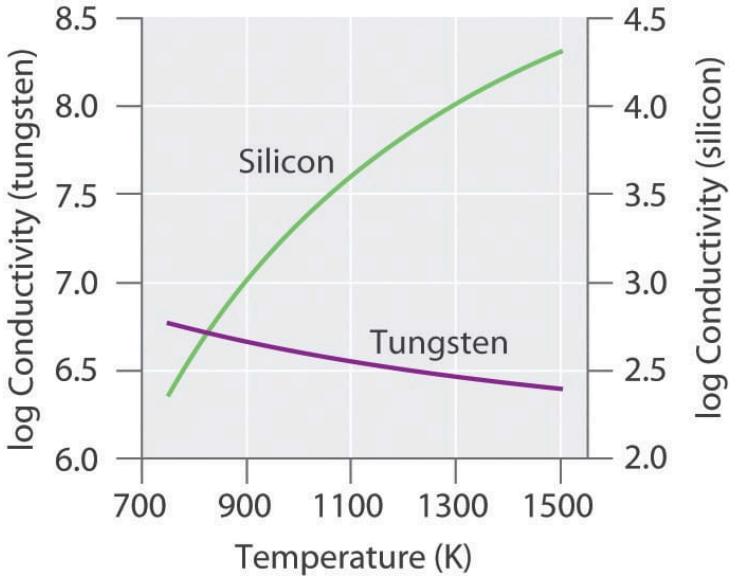


Figure 12.4.1.6: The Temperature Dependence of the Electrical Conductivity of a Metal versus a Semiconductor. The conductivity of the metal (tungsten) decreases relatively slowly with increasing temperature, whereas the conductivity of the semiconductor (silicon) increases much more rapidly.

n- and p-Type Semiconductors

Doping is a process used to tune the electrical properties of commercial semiconductors by deliberately introducing small amounts of impurities. If an impurity contains more valence electrons than the atoms of the host lattice (e.g., when small amounts of a group 15 atom are introduced into a crystal of a group 14 element), then the doped solid has more electrons available to conduct current than the pure host has. As shown in Figure 12.4.1.7*a*, adding an impurity such as phosphorus to a silicon crystal creates occasional electron-rich sites in the lattice. The electronic energy of these sites lies between those of the filled valence band and the empty conduction band but closer to the conduction band. Because the atoms that were introduced are surrounded by host atoms, and the electrons associated with the impurity are close in energy to the conduction band, those extra electrons are relatively easily excited into the empty conduction band of the host. Such a substance is called an n-type semiconductor, with the n indicating that the added charge carriers are negative (they are electrons).

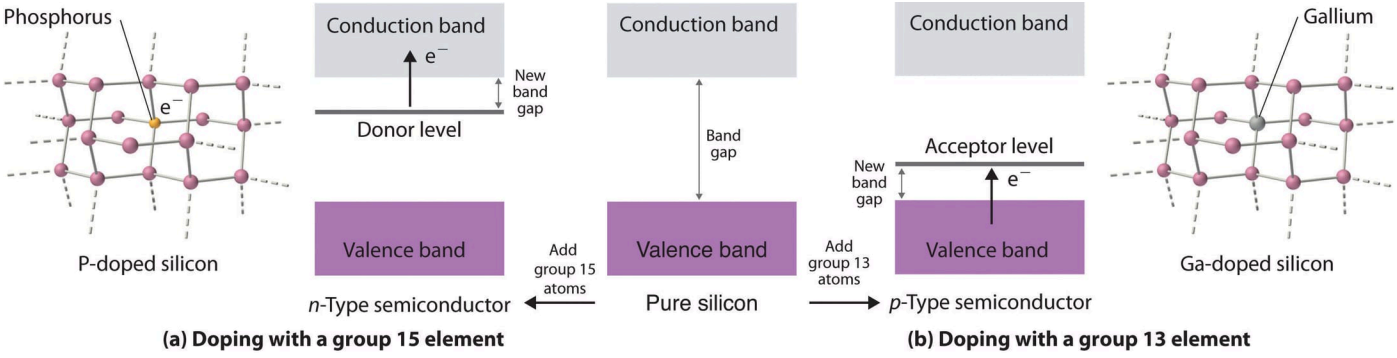


Figure 12.4.1.7: Structures and Band Diagrams of n-Type and p-Type Semiconductors. (a) Doping silicon with a group 15 element results in a new filled level between the valence and conduction bands of the host. (b) Doping silicon with a group 13 element results in a new empty level between the valence and conduction bands of the host. In both cases, the effective band gap is substantially decreased, and the electrical conductivity at a given temperature increases dramatically.

If the impurity atoms contain fewer valence electrons than the atoms of the host (e.g., when small amounts of a group 13 atom are introduced into a crystal of a group 14 element), then the doped solid has fewer electrons than the pure host. Perhaps unexpectedly, this also results in increased conductivity because the impurity atoms generate holes in the valence band. As shown in Figure 12.4.1.7*b*, adding an impurity such as gallium to a silicon crystal creates isolated electron-deficient sites in the host

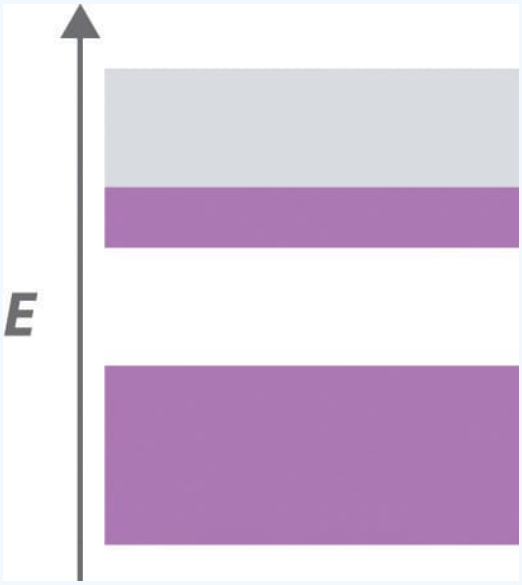
lattice. The electronic energy of these empty sites also lies between those of the filled valence band and the empty conduction band of the host but much closer to the filled valence band. It is therefore relatively easy to excite electrons from the valence band of the host to the isolated impurity atoms, thus forming holes in the valence band. This kind of substance is called a *p-type semiconductor,* with the p standing for positive charge carrier (i.e., a hole). Holes in what was a filled band are just as effective as electrons in an empty band at conducting electricity.

The electrical conductivity of a semiconductor is roughly proportional to the number of charge carriers, so doping is a precise way to adjust the conductivity of a semiconductor over a wide range. The entire semiconductor industry is built on methods for preparing samples of Si, Ge, or GaAs doped with precise amounts of desired impurities and assembling silicon chips and other complex devices with junctions between n- and p-type semiconductors in varying numbers and arrangements.

Because silicon does not stand up well to temperatures above approximately 100°C, scientists have been interested in developing semiconductors made from diamonds, a more thermally stable material. A new method has been developed based on vapor deposition, in which a gaseous mixture is heated to a high temperature to produce carbon that then condenses on a diamond kernel. This is the same method now used to create cultured diamonds, which are indistinguishable from natural diamonds. The diamonds are heated to more than 2000°C under high pressure to harden them even further. Doping the diamonds with boron has produced p-type semiconductors, whereas doping them with boron and deuterium achieves n-type behavior. Because of their thermal stability, diamond semiconductors have potential uses as microprocessors in high-voltage applications.

Example 12.4.1.1

A crystalline solid has the following band structure, with the purple areas representing regions occupied by electrons. The lower band is completely occupied by electrons, and the upper level is about one-third filled with electrons.



a. Predict the electrical properties of this solid.
b. What would happen to the electrical properties if all of the electrons were removed from the upper band? Would you use a chemical oxidant or reductant to effect this change?
c. What would happen to the electrical properties if enough electrons were added to completely fill the upper band? Would you use a chemical oxidant or reductant to effect this change?

Given: band structure

Asked for: variations in electrical properties with conditions

Strategy:

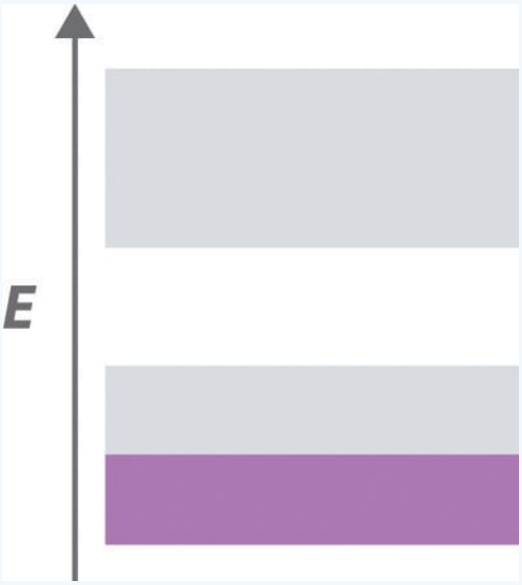
A. Based on the occupancy of the lower and upper bands, predict whether the substance will be an electrical conductor. Then predict how its conductivity will change with temperature.
B. After all the electrons are removed from the upper band, predict how the band gap would affect the electrical properties of the material. Determine whether you would use a chemical oxidant or reductant to remove electrons from the upper band.
C. Predict the effect of a filled upper band on the electrical properties of the solid. Then decide whether you would use an oxidant or a reductant to fill the upper band.

Solution:

A. The material has a partially filled band, which is critical for metallic behavior. The solid will therefore behave like a metal, with high electrical conductivity that decreases slightly with increasing temperature.
B. Removing all of the electrons from the partially filled upper band would create a solid with a filled lower band and an empty upper band, separated by an energy gap. If the band gap is large, the material will be an electrical insulator. If the gap is relatively small, the substance will be a semiconductor whose electrical conductivity increases rapidly with increasing temperature. Removing the electrons would require an oxidant because oxidants accept electrons.
C. Adding enough electrons to completely fill the upper band would produce an electrical insulator. Without another empty band relatively close in energy above the filled band, semiconductor behavior would be impossible. Adding electrons to the solid would require a reductant because reductants are electron donors.

Exercise 12.4.1.1

A substance has the following band structure, in which the lower band is half-filled with electrons (purple area) and the upper band is empty.



a. Predict the electrical properties of the solid.
b. What would happen to the electrical properties if all of the electrons were removed from the lower band? Would you use a chemical oxidant or reductant to effect this change?
c. What would happen to the electrical properties if enough electrons were added to completely fill the lower band? Would you use a chemical oxidant or reductant to effect this change?

Answer:

a. The solid has a partially filled band, so it has the electrical properties of a conductor.
b. Removing all of the electrons from the lower band would produce an electrical insulator with two empty bands. An oxidant is required.

c. Adding enough electrons to completely fill the lower level would result in an electrical insulator if the energy gap between the upper and lower bands is relatively large, or a semiconductor if the band gap is relatively small. A reductant is required.

- Metallic behavior requires a set of delocalized orbitals and a band of allowed energy levels that is partially occupied.
- The electrical conductivity of a semiconductor increases with increasing temperature, whereas the electrical conductivity of a metal decreases with increasing temperature.
- n-Type semiconductors are negative charge carriers; the impurity has more valence electrons than the host. p-Type semiconductors are positive charge carriers; the impurity has fewer valence electrons than the host.

Summary

Band theory assumes that the valence orbitals of the atoms in a solid interact to generate a set of molecular orbitals that extend throughout the solid; the continuous set of allowed energy levels is an energy band. The difference in energy between the highest and lowest allowed levels within a given band is the bandwidth, and the difference in energy between the highest level of one band and the lowest level of the band above it is the band gap. If the width of adjacent bands is larger than the energy gap between them, overlapping bands result, in which molecular orbitals derived from two or more kinds of valence orbitals have similar energies. Metallic properties depend on a partially occupied band corresponding to a set of molecular orbitals that extend throughout the solid to form a band of energy levels. If a solid has a filled valence band with a relatively low-lying empty band above it (a conduction band), then electrons can be excited by thermal energy from the filled band into the vacant band where they can then migrate through the crystal, resulting in electrical conductivity. Electrical insulators are poor conductors because their valence bands are full. Semiconductors have electrical conductivities intermediate between those of insulators and metals. The electrical conductivity of semiconductors increases rapidly with increasing temperature, whereas the electrical conductivity of metals decreases slowly with increasing temperature. The properties of semiconductors can be modified by doping, or introducing impurities. Adding an element with more valence electrons than the atoms of the host populates the conduction band, resulting in an n-type semiconductor with increased electrical conductivity. Adding an element with fewer valence electrons than the atoms of the host generates holes in the valence band, resulting in a p-type semiconductor that also exhibits increased electrical conductivity.

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12.4.2: Silicon Devices

Introduction

The synthesis and purification of bulk polycrystalline semiconductor material represents the first step towards the commercial fabrication of an electronic device. This polycrystalline material is then used as the raw material for the formation of single crystal material that is processed to semiconductor wafers. The strong influence on the electric characteristics of a semiconductors exhibited by small amounts of some impurities requires that the bulk raw material be of very high purity (> 99.9999%). Although some level of purification is possible during the crystallization process it is important to use as high a purity starting material as possible.

Following oxygen (46%), silicon (L. silicis flint) is the most abundant element in the earth's crust (28%). However, silicon does not occur in its elemental form, but as its oxide (SiO_2) or as silicates. Sand, quartz, amethyst, agate, flint, and opal are some of the forms in which the oxide appears. Granite, hornblende, asbestos, feldspar, clay and mica, etc. are a few of the numerous silicate minerals. With such boundless supplies of the raw material, the costs associated with the production of bulk silicon is not one of abstraction and conversion of the oxide(s), but of purification of the crude elemental silicon. While 98% elemental silicon, known as metallurgical-grade silicon (MGS), is readily produced on a large scale, the requirements of extreme purity for electronic device fabrication require additional purification steps in order to produce electronic-grade silicon (EGS). Electronic-grade silicon is also known as semiconductor-grade silicon (SGS). In order for the purity levels to be acceptable for subsequent crystal growth and device fabrication, EGS must have carbon and oxygen impurity levels less than a few parts per million (ppm), and metal impurities at the parts per billion (ppb) range or lower. Table 12.4.2.1 and Table 12.4.2.2 give typical impurity concentrations in MGS and EGS, respectively. Besides the purity, the production cost and the specifications must meet the industry desires.

Table 12.4.2.1: Typical impurity concentrations found in metallurgical-grade silicon (MGS).

Element	Concentration (ppm)	Element	Concentration (ppm)
aluminum	1000-4350	manganese	50-120
boron	40-60	molybdenum	< 20
calcium	245-500	nickel	10-105
chromium	50-200	phosphorus	20-50
copper	15-45	titanium	140-300
iron	1550-6500	vanadium	50-250
magnesium	10-50	zirconium	20

Table 12.4.2.2: Typical impurity concentrations found in electronic-grade silicon (EGS).

Element	Concentration (ppb)	Element	Concentration (ppb)
arsenic	< 0.001	gold	< 0.00001
antimony	< 0.001	iron	0.1-1.0
boron	≤ 0.1	nickel	0.1-0.5
carbon	100-1000	oxygen	100-400
chromium	< 0.01	phosphorus	≤ 0.3
cobalt	0.001	silver	0.001
copper	0.1	zinc	< 0.1

Metallurgical-grade silicon (MGS)

The typical source material for commercial production of elemental silicon is quartzite gravel; a relatively pure form of sand (SiO_2). The first step in the synthesis of silicon is the melting and reduction of the silica in a submerged-electrode arc furnace. An example of which is shown schematically in Figure 12.4.2.1, along with the appropriate chemical reactions. A mixture of quartzite gravel and carbon are heated to high temperatures (ca. 1800 °C) in the furnace. The carbon bed consists of a mixture of coal, coke, and wood chips. The latter providing the necessary porosity such that the gases created during the reaction (SiO and CO) are able to flow through the bed.

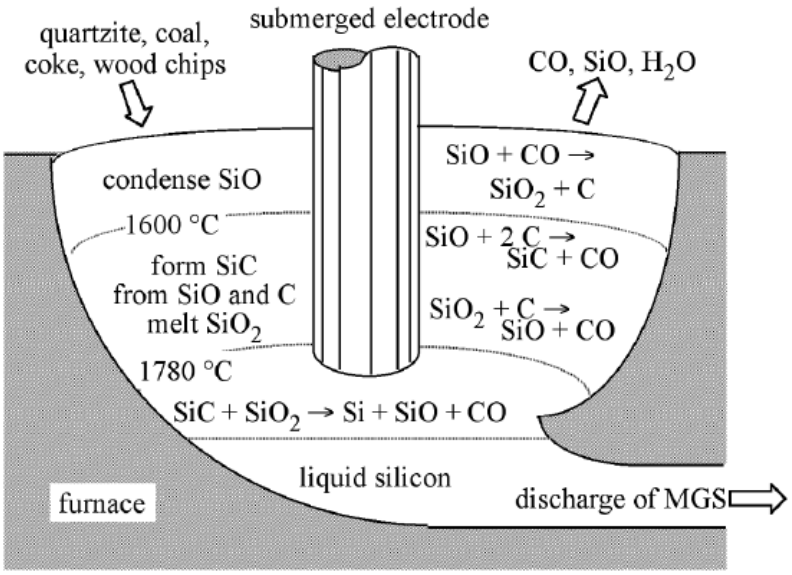


Figure 12.4.2.1: Schematic of submerged-electrode arc furnace for the production of metallurgical-grade silicon (MGS).

The overall reduction reaction of SiO_2 is expressed in (7.10.1), however, the reaction sequence is more complex than this overall reaction implies, and involves the formation of SiC and SiO intermediates. The initial reaction between molten SiO_2 and C, (7.10.2), takes place in the arc between adjacent electrodes, where the local temperature can exceed 2000 °C. The SiO and CO thus generated flow to cooler zones in the furnace where SiC is formed, (7.10.3), or higher in the bed where they reform SiO_2 and C, (7.10.2). The SiC reacts with molten SiO_2, (7.10.4), producing the desired silicon along with SiO and CO. The molten silicon formed is drawn-off from the furnace and solidified.

$$\mathrm{SiO_2(liquid) + 2\ C(solid) \rightarrow Si(liquid) + 2\ CO(gas)}$$

$$\mathrm{SiO_2 + 2\ C \underset{<1600\ ^\circ C}{\overset{>1700\ ^\circ C}{\rightleftharpoons}} SiO + CO}$$

$$\mathrm{SiO + 2C \rightarrow SiC + CO\ (1600\text{ - }1700\ ^\circ C)}$$

'_' allowed only in math mode

The as-produced MGS is approximately 98-99% pure, with the major impurities being aluminum and iron (Table 12.4.2.1), however, obtaining low levels of boron impurities is of particular importance, because it is difficult to remove and serves as a dopant for silicon. The drawbacks of the above process are that it is energy and raw material intensive. It is estimated that the production of one metric ton (1,000 kg) of MGS requires 2500 - 2700 kg quartzite, 600 kg charcoal, 600 - 700 kg coal or coke, 300 - 500 kg wood chips, and 500,000 kWh of electric power. Currently, approximately 500,000 metric tons of MGS are produced per year, worldwide. Most of the production (ca. 70%) is used for metallurgical applications (e.g., aluminum-silicon alloys are commonly used for automotive engine blocks) from whence its name is derived. Applications in a variety of chemical products such as silicone resins account for about 30%, and only 1% or less of the total production of MGS is used in the manufacturing of high-purity EGS for the electronics industry. The current worldwide consumption of EGS is approximately 5 x 10^6 kg per year.

Electronic-grade silicon (EGS)

Electronic-grade silicon (EGS) is a polycrystalline material of exceptionally high purity and is the raw material for the growth of single-crystal silicon. EGS is one of the purest materials commonly available, see Table 12.4.2.2. The formation of EGS from MGS is accomplished through chemical purification processes. The basic concept of which involves the conversion of MGS to a volatile silicon compound, which is purified by distillation, and subsequently decomposed to re-form elemental silicon of higher purity (i.e., EGS). Irrespective of the purification route employed, the first step is physical pulverization of MGS followed by its conversion to the volatile silicon compounds.

A number of compounds, such as monosilane (SiH_4), dichlorosilane (SiH_2Cl_2), trichlorosilane ($SiHCl_3$), and silicon tetrachloride ($SiCl_4$), have been considered as chemical intermediates. Among these, $SiHCl_3$ has been used predominantly as the intermediate compound for subsequent EGS formation, although SiH_4 is used to a lesser extent. Silicon tetrachloride and its lower chlorinated derivatives are used for the chemical vapor deposition (CVD) growth of Si and SiO_2. The boiling points of silane and its chlorinated products (Table 12.4.2.3) are such that they are conveniently separated from each other by fractional distillation.

Table 12.4.2.3: Boiling points of silane and chlorosilanes at 760 mmHg (1 atmosphere).

Compound	Boiling point (°C)
SiH_4	-112.3
SiH_3Cl	-30.4
SiH_2Cl_2	8.3
$SiHCl_3$	31.5
$SiCl_4$	57.6

The reasons for the predominant use of $SiHCl_3$ in the synthesis of EGS are as follows:

1. $SiHCl_3$ can be easily formed by the reaction of anhydrous hydrogen chloride with MGS at reasonably low temperatures (200 - 400 °C);
2. it is liquid at room temperature so that purification can be accomplished using standard distillation techniques;
3. it is easily handled and if dry can be stored in carbon steel tanks;
4. its liquid is easily vaporized and, when mixed with hydrogen it can be transported in steel lines without corrosion;
5. it can be reduced at atmospheric pressure in the presence of hydrogen;
6. its deposition can take place on heated silicon, thus eliminating contact with any foreign surfaces that may contaminate the resulting silicon; and
7. it reacts at lower temperatures (1000 - 1200 °C) and at faster rates than does $SiCl_4$.

Chlorosilane (Seimens) process

Trichlorosilane is synthesized by heating powdered MGS with anhydrous hydrogen chloride (HCl) at around 300 °C in a fluidized-bed reactor, (7.10.5).

'_' allowed only in math mode

Since the reaction is actually an equilibrium and the formation of $SiHCl_3$ highly exothermic, efficient removal of generated heat is essential to assure a maximum yield of $SiHCl_3$. While the stoichiometric reaction is that shown in (7.10.5), a mixture of chlorinated silanes is actually prepared which must be separated by fractional distillation, along with the chlorides of any impurities. In particular iron, aluminum, and boron are removed as $FeCl_3$ (b.p. = 316 °C), $AlCl_3$ (m.p. = 190 °C subl.), and BCl_3 (b.p. = 12.65 °C), respectively. Fractional distillation of $SiHCl_3$ from these impurity halides result in greatly increased purity with a concentration of electrically active impurities of less than 1 ppb.

EGS is prepared from purified $SiHCl_3$ in a chemical vapor deposition (CVD) process similar to the epitaxial growth of Si. The high-purity $SiHCl_3$ is vaporized, diluted with high-purity hydrogen, and introduced into the Seimens deposition reactor, shown schematically in Figure 12.4.2.2. Within the reactor, thin silicon rods called slim rods (ca. 4 mm diameter) are supported by graphite electrodes. Resistance heating of the slim rods causes the decomposition of the $SiHCl_3$ to yield silicon, as described by

the reverse reaction shown in (7.10.5).

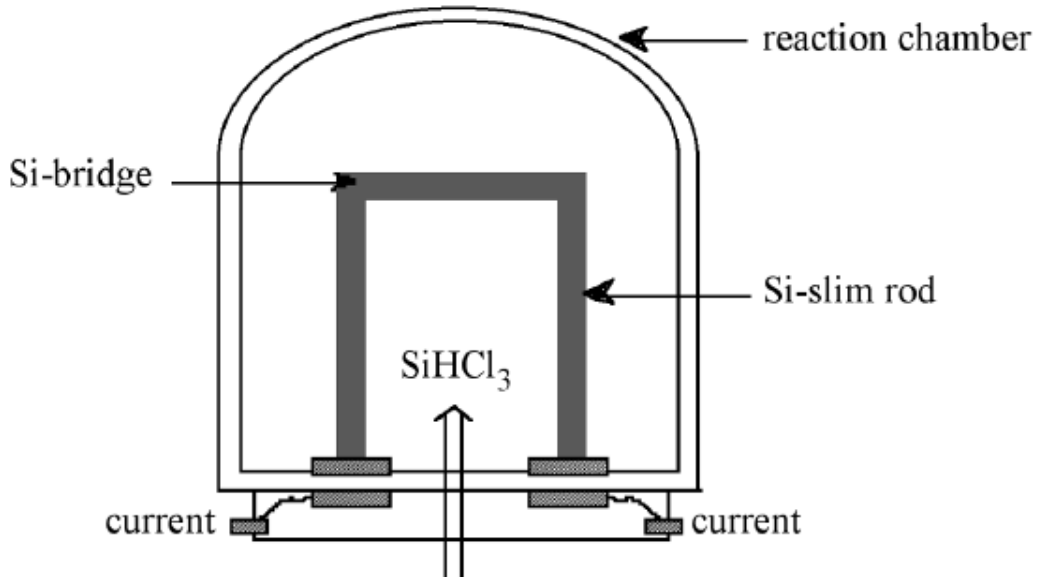


Figure 12.4.2.2: Schematic representation of a Seimens deposition reactor.

The shift in the equilibrium from forming $SiHCl_3$ from Si at low temperature, to forming Si from $SiHCl_3$ at high temperature is as a consequence of the temperature dependence, (7.10.6), of the equilibrium constant, (7.10.7) where ρ = partial pressure, for (7.10.5). Since the formation of $SiHCl_3$ is exothermic, i.e., $\Delta H < 0$, an increase in the temperature causes the partial pressure of $SiHCl_3$ to decrease. Thus, the Siemens process is typically run at ca. 1100 °C, while the reverse fluidized bed process is carried out at 300 °C.

$$\ln K_p = \frac{-\Delta H}{RT}$$

$$K_p = \frac{{}^{\rho}SiHCl_3 \; {}^{\rho}H_2}{{}^{\rho}HCl}$$

The slim rods act as a nucleation point for the deposition of silicon, and the resulting polycrystalline rod consists of columnar grains of silicon (polysilicon) grown perpendicular to the rod axis. Growth occurs at less than 1 mm per hour, and after deposition for 200 to 300 hours high-purity (EGS) polysilicon rods of 150 - 200 mm in diameter are produced. For subsequent float-zone refining the polysilicon EGS rods are cut into long cylindrical rods. Alternatively, the as-formed polysilicon rods are broken into chunks for single crystal growth processes, for example Czochralski melt growth.

In addition to the formation of silicon, the HCl coproduct reacts with the $SiHCl_3$ reactant to form silicon tetrachloride ($SiCl_4$) and hydrogen as major byproducts of the process, (7.10.8). This reaction represents a major disadvantage with the Seimens process: poor efficiency of silicon and chlorine consumption. Typically, only 30% of the silicon introduced into CVD reactor is converted into high-purity polysilicon.

$$HCl + SiHCl_3 \rightarrow SiCl_4 + H_2$$

In order to improve efficiency the HCl, $SiCl_4$, H_2, and unreacted $SiHCl_3$ are separated and recovered for recycling. Figure 12.4.2.3 illustrates the entire chlorosilane process starting with MGS and including the recycling of the reaction byproducts to achieve high overall process efficiency. As a consequence, the production cost of high-purity EGS depends on the commercial usefulness of the byproduct, $SiCl_4$. Additional disadvantages of the Seimens process are derived from its relatively small batch size, slow growth rate, and high power consumption. These issues have lead to the investigation of alternative cost efficient routes to EGS.

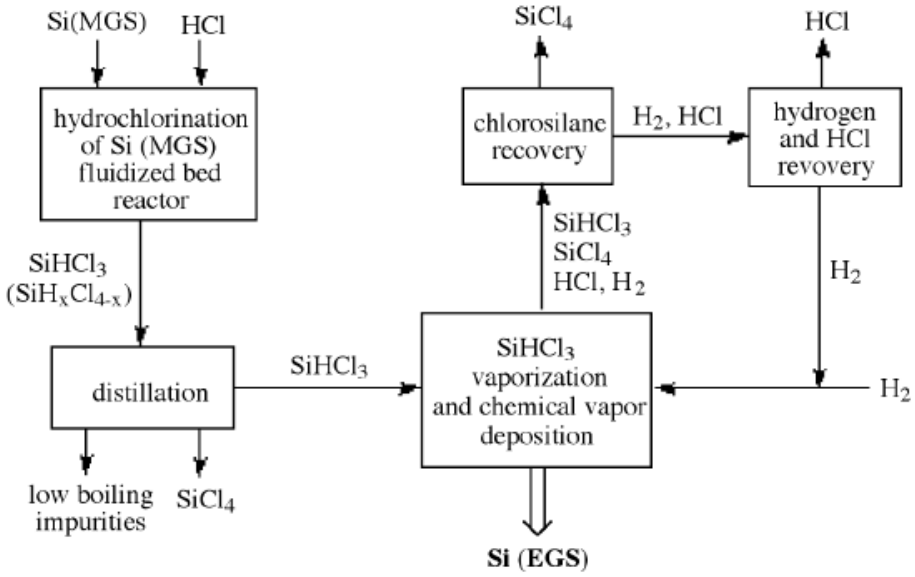


Figure 12.4.2.3: Schematic representation of the reaction pathways for the formation of EGS using the chlorosilane process.

Silane process

An alternative process for the production of EGS that has begun to receive commercial attention is the pyrolysis of silane (SiH_4). The advantages of producing EGS from SiH_4 instead of $SiHCl_3$ are potentially lower costs associated with lower reaction temperatures, and less harmful byproducts. Silane decomposes < 900 °C to give silicon and hydrogen, (7.10.9).

$$SiH_4(vapor) \rightarrow Si(solid) + 2\ H_2(gas)$$

Silane may be prepared by a number of routes, each having advantages with respect to purity and production cost. The simplest process involves the direct reaction of MGS powders with magnesium at 500 °C in a hydrogen atmosphere, to form magnesium silicide (Mg_2Si). The magnesium silicide is then reacted with ammonium chloride in liquid ammonia below 0 °C, (7.10.10).

$$Mg_2Si + 4\ NH_4Cl \rightarrow SiH_4 + 2\ MgCl_2 + 5\ NH_3$$

This process is ideally suited to the removal of boron impurities (a p-type dopant in Si), because the diborane (B_2H_6) produced during the reaction forms the Lewis acid-base complex, $H_3B(NH_3)$, whose volatility is sufficiently lower than SiH_4, allowing for the purification of the latter. It is possible to prepare EGS with a boron content of ≤ 20 ppt using SiH_4 synthesized in this manner. However, phosphorus (another dopant) in the form of PH_3 may be present as a contaminant requiring subsequent purification of the SiH_4.

Alternative routes to SiH_4 involve the chemical reduction of $SiCl_4$ by either lithium hydride, (7.10.11), lithium aluminum hydride, (7.10.12), or via hydrogenation in the presence of elemental silicon, (7.10.13) - (7.10.16). The hydride reduction reactions may be carried-out on relatively large scales (ca. 50 kg), but only batch processes. In contrast, Union Carbide has adapted the hydrogenation to a continuous process, involving disproportionation reactions of chlorosilanes, (7.10.14) - (7.10.16), and the fractional distillation of silane, Table 12.4.2.3.

$$SiCl_4 + LiH \rightarrow SiH_4 + 4\ LiCl$$

$$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + LiCl + AlCl_4$$

$$SiCl_4 + 2\ H_2 + Si(98 \rightarrow 4\ SiHCl_3$$

$$2\ SiHCl_3 \rightarrow SiH_2Cl_2 + 2\ SiHCl_3$$

$$3\ SiH_2Cl_2 \rightarrow SiH_2Cl + 2\ SiHCl_3$$

$$2\ SiH_3Cl \rightarrow SiH_4 + SiH_2Cl_2$$

Pyrolysis of silane on resistively heated polysilicon filaments at 700 - 800 °C yields polycrystalline EGS. As noted above, the EGS formed has remarkably low boron impurities compared with material prepared from trichlorosilane. Moreover, the resulting EGS is less contaminated with transition metals from the reactor container because SiH_4 decomposition does not cause as much of a corrosion problem as is observed with halide precursor compounds.

Granular polysilicon deposition

Both the chlorosilane (Seimens) and silane processes result in the formation of rods of EGS. However, there has been increased interest in the formation of granular polycrystalline EGS. This process was developed in 1980's, and relies on the decomposition of SiH_4 in a fluidized-bed deposition reactor to produce free-flowing granular polysilicon.

Tiny silicon particles are fluidized in a SiH_4/H_2 flow, and act as seed crystal onto which polysilicon deposits to form free-flowing spherical particles. The size distribution of the particles thus formed is over the range from 0.1 to 1.5 mm in diameter with an average particle size of 0.7 mm. The fluidized-bed seed particles are originally made by grinding EGS in a ball (or hammer) mill and leaching the product with acid, hydrogen peroxide, and water. This process is time-consuming and costly, and tended to introduce undesirable impurities from the metal grinders. In a new method, large EGS particles are fired at each other by a high-speed stream of inert gas and the collision breaks them down into particles of suitable size for a fluidized bed. This process has the main advantage that it introduces no foreign materials and requires no leaching or other post purification.

The fluidized-bed reactors are much more efficient than traditional rod reactors as a consequence of the greater surface area available during CVD growth of silicon. It has been suggested that fluidized-bed reactors require $^1/_5$ to $^1/_{10}$ the energy, and half the capital cost of the traditional process. The quality of fluidized-bed polysilicon has proven to be equivalent to polysilicon produced by the conventional methods. Moreover, granular EGS in a free-flowing form, and with high bulk density, enables crystal growers to obtain the high, reproducible production yields out of each crystal growth run. For example, in the Czochralski crystal growth process, crucibles can be quickly and easily filled to uniform loading with granular EGS, which typically exceed those of randomly stacked polysilicon chunks produced by the Siemens silane process.

Zone refining

The technique of zone refining is used to purify solid materials and is commonly employed in metallurgical refining. In the case of silicon may be used to obtain the desired ultimate purity of EGS, which has already been purified by chemical processes. Zone refining was invented by Pfann, and makes use of the fact that the equilibrium solubility of any impurity (e.g., Al) is different in the solid and liquid phases of a material (e.g., Si). For the dilute solutions, as is observed in EGS silicon, an equilibrium segregation coefficient (k_0) is defined by $k_0 = C_s/C_l$, where C_s and C_l are the equilibrium concentrations of the impurity in the solid and liquid near the interface, respectively.

If k_0 is less than 1 then the impurities are left in the melt as the molten zone is moved along the material. In a practical sense a molten zone is established in a solid rod. The zone is then moved along the rod from left to right. If $k_0 < 1$ then the frozen part left on the trailing edge of the moving molten zone will be purer than the material that melts in on the right-side leading edge of the moving molten zone. Consequently the solid to the left of the molten zone is purer than the solid on the right. At the completion of the first pass the impurities become concentrated to the right of the solid sample. Repetition of the process allows for purification to exceptionally high levels. Table 12.4.2.4 lists the equilibrium segregation coefficients for common impurity and dopant elements in silicon; it should be noted that they are all less than 1.

Table 12.4.2.4: Segregation coefficients for common impurity and dopant elements in silicon.

Element	k_0	Element	k_0
aluminum	0.002	iron	8×10^{-6}
boron	0.8	oxygen	0.25
carbon	0.07	phosphorus	0.35
copper	4×10^{-6}	antimony	0.023

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12.5: Materials for Optics

can be widely defined as an . An can be considered to have a random arrangement of , such as observed in a gas, but more realistically can considered to only lack long-range order such as those found in crystalline solids. is clear (optically transparent) silica which is composed largely of silicon dioxide (SiO). The definition of does not restrict either the composition or the optical properties of the material, implying a wide variety of different materials that are considered . In fact, theoretically, any crystalline solid that can be brought to a liquid state, can be forced into an state through rapid solidification via extraordinary cooling rates. This is easily observable by recognizing that quartz, a very common crystalline solid, has the same composition as silica (SiO) but was cooled slowly enough to form long-range order. Non-silica glasses, in particular metallic glasses, can obtain unique electric, optical, or thermal properties from their crystalline counterparts through glassification. Non-metallic glasses can obtain similarly unique properties by adjusting elemental compositions and introducing dopants. has been desirable for its optical properties since silica is transparent in the visible spectrum. Although there are crystalline materials that are similarly transparent (quartz), they have several properties which make them undesirable as optical media in many cases; though each grain may be transparent, grain boundaries reflect and/or scatter light in poly crystalline materials; unless cut along specific planes, the faces of crystals are forced to conform to a rigid geometric order which may also scatter light. Silica is not restricted by these constraints and has properties making it even more desirable both in terms of clarity and malleability; being unrestricted by a defined internal structure, the surface of is molecularly smooth, bound only by , even along curved faces. This is particularly important since most optical instruments (microscopes, telescopes, and eyeglasses) require smooth curved surfaces. isn't the only the fits the profile for optical functions. Acrylic , poly(methyl methacrylate), is a polymer, fitting the description of by being an . Acrylic has a very similar refractive index to silica (~1.5) and is physically lighter, softer, and more shatter-resistant than . Polycarbonates is another class of optically transparent polymers. It has even more desirable physical properties than acrylic in terms of strength and impact resistance. , in particular the index of refraction, can be modified by doping the . Doping the with low density materials such as boron can lower the index of refraction. Similarly, doping the material with higher density dopants, such as oxides of lead, titanium, barium or zirconium, can drastically increase the index of refraction. Glasses made or doped with germanium or phosphates are vitally important in the field ofFiber Optics. filters are often made of chalcogenide , composed of two non-oxygen group 16 elements (sulfur, selenium, tellurium) and one group 14 element (silicon, tin, lead) or group 15 element (phosphorus, arsenic, antimony, bismuth) in its most simple form. Often the size of the allow for leniency to create more complex amorphous chalcogenide glasses involving several different elements in compositions that only roughly match the two to one ratio of silica. These materials transmit only in the IR or near IR range, appearing black or faintly blue, while still having similar malleability of silica . Example IR filter chalcogenide glasses include AsSe, GeAsSe, and GeAsSeTe. is a well-known insulator, having a resistivity on the order of 10 ohm m. is especially desirable in the field of for its insulating properties; in device fabrication, is deposited between metals or as very thin insulators. Doped , such as phosphosilicate (phosphorus doped) or borophosphosilicate (boron and phosphorus doped) are often used instead of pure silica for their lower melting temperatures and increased planarization (forming smooth flat surfaces). The addition of fluorine, a highly electronegative element, into the can lower the and thus the dielectric constant of the , making it more desirable for integrated circuits. The addition of large , such as lead (II) oxide, can reduce the mobility of other significantly increasing the resistivity of the material. It's possible to give silica a level of electrical conductivity by dissolving small alkali metal into the , which have high mobility's at increasing temperatures. is commonly considered to be very susceptible to thermal shock and breaks or cracks easily when suddenly changing temperatures. This is true for the cheapest and most common form of which is soda-lime-silica , which contains roughly 30% sodium oxide (NaO), lime (CaO), magnesia (MgO) and alumina (AlO). Soda-lime has a of thermal expansion of 93.5E-7 cm/cm.°C, which describes the relative increase in size per degree Celsius change in temperature. Pure or nearly pure (~96%) silica has a small of thermal expansion of 7.5E-7 cm/cm.°C due to the homogeneity of the solid. Silica also has a significantly higher melting temperature, combined with the purity requirements, this makes it more expensive to produce. Borosilicate (~13% BO) is a very common form of used in cookware for its thermal shock resistance, having a of 35E-7 cm/cm.°C. Unlike pure silica , borosilicate is cheaper to produce, having a lower melting temperature and having less stringent purity requirements. Corning has developed glasses with ultra-low thermal expansion coefficients with values on the order of 10 cm/cm.°C. does play a huge role in thermal insulation in the form of fiber and wool. wool involves the production of very thin strands on soda-lime to form a low density packing material. wool can achieve higher specific heats than either or water on the order of 7 J/g.K. requires massive cooling rates, on the order of 10 K/s. These cooling rates can be achieved by a variety of methods including:

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12.6: Materials for Nanotechnology

Inorganic nanomaterials, (e.g. quantum dots, nanowires and nanorods) because of their interesting optical and electrical properties, could be used in optoelectronics. Furthermore, the optical and electronic properties of nanomaterials which depend on their size and shape can be tuned via synthetic techniques. There are the possibilities to use those materials in organic material based optoelectronic devices such as Organic solar cells, OLEDs etc. The operating principles of such devices are governed by photoinduced processes like electron transfer and energy transfer. The performance of the devices depends on the efficiency of the photoinduced process responsible for their functioning. Therefore, better understanding of those photoinduced processes in organic/inorganic nanomaterial composite systems is necessary in order to use them in organic optoelectronic devices.

Nanoparticles or nanocrystals made of metals, semiconductors, or oxides are of particular interest for their mechanical, electrical, magnetic, optical, chemical and other properties. Nanoparticles have been used as quantum dots and as chemical catalysts such as nanomaterial-based catalysts. Recently, a range of nanoparticles are extensively investigated for biomedical applications including tissue engineering, drug delivery, biosensor.

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials.

Nanoparticles exhibit a number of special properties relative to bulk material. For example, the bending of bulk copper (wire, ribbon, etc.) occurs with movement of copper atoms/clusters at about the 50 nm scale. Copper nanoparticles smaller than 50 nm are considered super hard materials that do not exhibit the same malleability and ductility as bulk copper. The change in properties is not always desirable. Ferroelectric materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them useless for memory storage. Suspensions of nanoparticles are possible because the interaction of the particle surface with the solvent is strong enough to overcome differences in density, which usually result in a material either sinking or floating in a liquid. Nanoparticles often have unexpected visual properties because they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep red to black in solution.

The often very high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering is possible at lower temperatures and over shorter durations than for larger particles. This theoretically does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate do complicate matters. The surface effects of nanoparticles also reduces the incipient melting temperature.

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13: PROPERTIES OF SOLUTIONS

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent.

13.1: The Solution Process

13.2: Saturated Solutions and Solubility

13.3: Factors Affecting Solubility

13.4: Ways of Expressing Concentration

13.5: Colligative Properties

13.6: Colloids

13.E: Properties of Solutions (Exercises)

13.S: Properties of Solutions (Summary)

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13.1: The Solution Process

Learning Objectives

- To understand how enthalpy and entropy changes affect solution formation.
- To use the magnitude of the changes in both enthalpy and entropy to predict whether a given solute–solvent combination will spontaneously form a solution.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent. Table $13.1.1$ lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table $13.1.1$*: Types of Solutions*

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)
solid	solid	solid	alloys and other "solid solutions"

Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$$\mathrm{Zn(NO_3)_2\,(s) + H_2O\,(l)\ \rightarrow Zn^{2+}\,(aq) + 2\,NO_3^-\,(aq)} \tag{13.1.1}$$

Because $Zn(NO_3)_2$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq)\ \rightarrow Zn^{2+}\,(aq) + 2\,Cl^-\,(aq) + H_2\,(g)} \tag{13.1.2}$$

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation (that it is a physical change).

> Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.

Substances that form a single homogeneous phase in all proportions are said to be completely *miscible* in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are *immiscible*. Examples of gaseous solutions that we have already discussed include Earth's atmosphere.

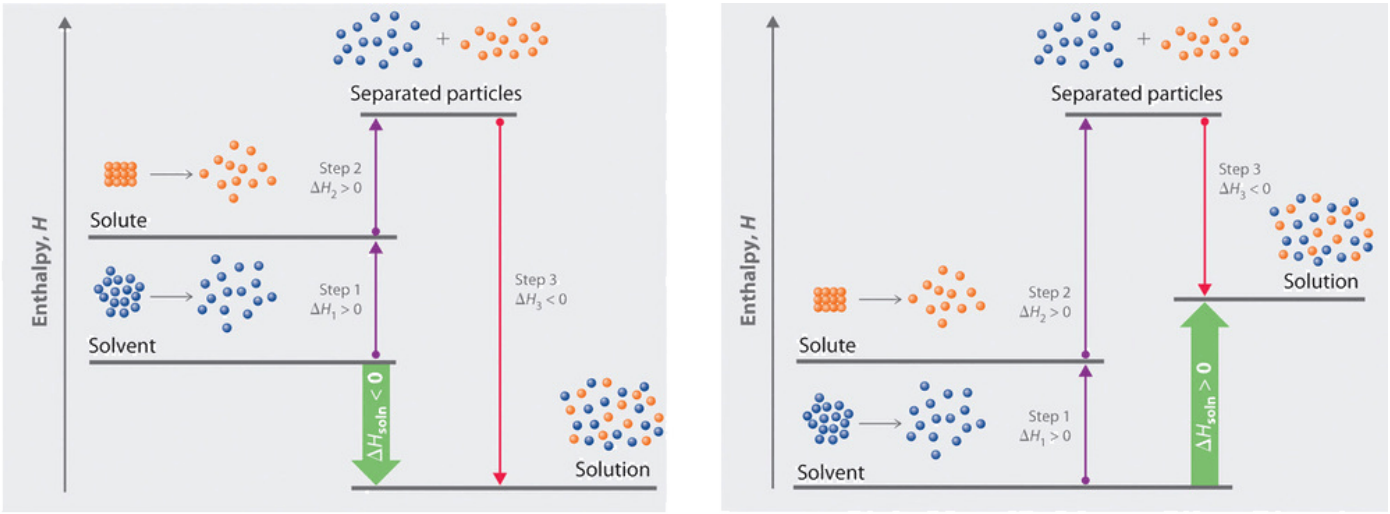
The Role of Enthalpy in Solution Formation

Energy is required to overcome the intermolecular interactions in a solute, which can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called solvation (or hydration when the solvent is water). Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use a thermochemical cycle to analyze the energetics of solution formation. The process occurs in three discrete steps, indicated by ΔH_1, ΔH_2, and ΔH_3 in Figure 13.1.2. The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{13.1.3}$$

When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent (ΔH_1) and the solute (ΔH_2). Because ΔH is positive for both steps 1 and 2, the solute–solvent interactions (ΔH_3) must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic ($\Delta H_{soln} < 0$). When the solute is an ionic solid, ΔH_2 corresponds to the lattice energy that must be overcome to form a solution. The higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as MgO (–3791 kJ/mol), are generally insoluble in all solvents.



(a) Exothermic solution formation **(b) Endothermic solution formation**

Figure 13.1.2: Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is exothermic ($\Delta H_{soln} < 0$), as shown in the thermochemical cycle. (b) When ΔH_3 is smaller in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is endothermic ($\Delta H_{soln} > 0$).

A positive value for ΔH_{soln} does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high ΔH_{soln} is usually an indication that the substance is not very soluble. Instant cold packs used to treat athletic injuries, for example, take advantage of the large positive ΔH_{soln} of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure 13.1.3).



Figure 13.1.3: Commercial Cold Packs for Treating Injuries. These packs contain solid NH_4NO_3 and water in separate compartments. When the seal between the compartments is broken, the NH_4NO_3 dissolves in the water. Because ΔH_{soln} for NH_4NO_3 is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

Entropy and Solution Formation

The enthalpy change that accompanies a process is important because processes that release substantial amounts of energy tend to occur spontaneously. A second property of any system, its entropy, is also important in helping us determine whether a given process occurs spontaneously. We will discuss entropy in more detail elsewhere, but for now we can state that entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. A perfect crystal at 0 K, whose atoms are regularly arranged in a perfect lattice and are motionless, has an entropy of zero. In contrast, gases have large positive entropies because their molecules are highly disordered and in constant motion at high speeds.

The formation of a solution disperses molecules, atoms, or ions of one kind throughout a second substance, which generally increases the disorder and results in an increase in the entropy of the system. Thus entropic factors almost always favor formation of a solution. In contrast, a change in enthalpy may or may not favor solution formation. The London dispersion forces that hold cyclohexane and n-hexane together in pure liquids, for example, are similar in nature and strength. Consequently, ΔH_{soln} should be approximately zero, as is observed experimentally. Mixing equal amounts of the two liquids, however, produces a solution in which the n-hexane and cyclohexane molecules are uniformly distributed over approximately twice the initial volume. In this case, the driving force for solution formation is not a negative ΔH_{soln} but rather the increase in entropy due to the increased disorder in the mixture. All spontaneous processes with $\Delta H \geq 0$ are characterized by an *increase* in entropy. In other cases, such as mixing oil with water, salt with gasoline, or sugar with hexane, the enthalpy of solution is large and positive, and the increase in entropy resulting from solution formation is not enough to overcome it. Thus in these cases a solution does not form.

> All spontaneous processes with ΔH ≥ 0 are characterized by an increase in entropy.

Table 13.1.2 summarizes how enthalpic factors affect solution formation for four general cases. The column on the far right uses the relative magnitudes of the enthalpic contributions to predict whether a solution will form from each of the four. Keep in mind that in each case entropy favors solution formation. In two of the cases the enthalpy of solution is expected to be relatively small and can be either positive or negative. Thus the entropic contribution dominates, and we expect a solution to form readily. In the other two cases the enthalpy of solution is expected to be large and positive. The entropic contribution, though favorable, is usually too small to overcome the unfavorable enthalpy term. Hence we expect that a solution will not form readily.

*Table 13.1.2: Relative Changes in Enthalpies for Different Solute–Solvent Combinations**

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} (ΔH_1 + ΔH_2 +ΔH_3)	Result of Mixing Solute and Solvent†
large; positive	large; positive	large; negative	small; positive or negative	solution will usually form

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} (ΔH_1 + ΔH_2 +ΔH_3)	Result of Mixing Solute and Solvent†
small; positive	large; positive	small; negative	large; positive	solution will not form
large; positive	small; positive	small; negative	large; positive	solution will not form
small; positive	small; positive	small; negative	small; positive or negative	solution will usually form

*ΔH_1, ΔH_2, and ΔH_3 refer to the processes indicated in the thermochemical cycle shown in Figure 13.1.2.
†In all four cases, entropy increases.

In contrast to liquid solutions, the intermolecular interactions in gases are weak (they are considered to be nonexistent in ideal gases). Hence mixing gases is usually a thermally neutral process ($\Delta H_{soln} \approx 0$), and the entropic factor due to the increase in disorder is dominant (Figure 13.1.4). Consequently, all gases dissolve readily in one another in all proportions to form solutions.

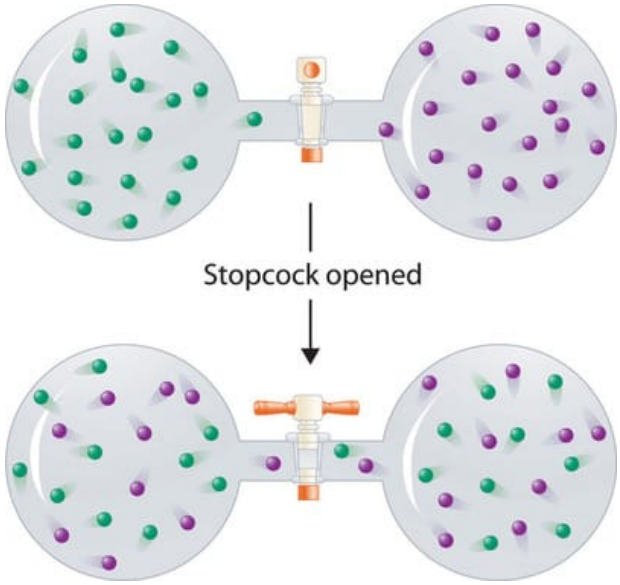
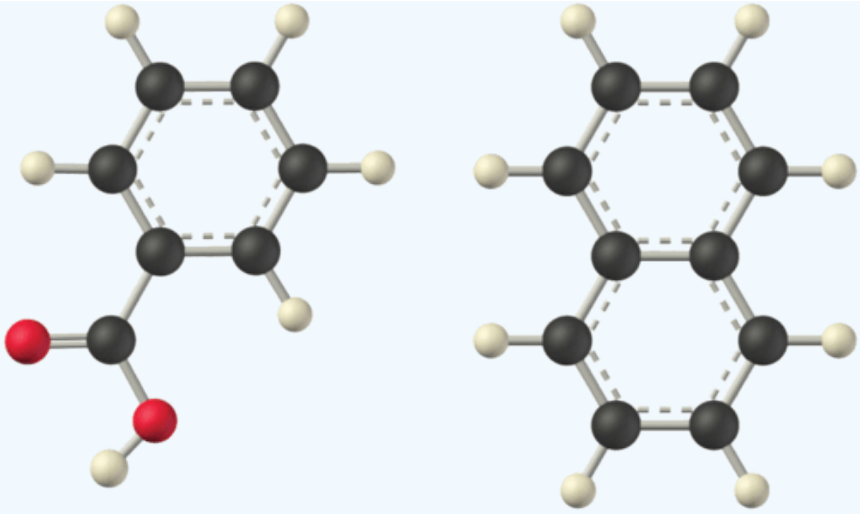


Figure 13.1.4: Formation of a Solution of Two Gases. (top) Pure samples of two different gases are in separate bulbs. (bottom) When the connecting stopcock is opened, diffusion causes the two gases to mix together and form a solution. Even though ΔH_{soln} is zero for the process, the increased entropy of the solution (the increased disorder) versus that of the separate gases favors solution formation.

Example 13.1.1

Considering LiCl, benzoic acid ($\mathrm{C_6H_5CO_2H}$), and naphthalene, which will be most soluble and which will be least soluble in water?



Given: three compounds

Asked for: relative solubilities in water

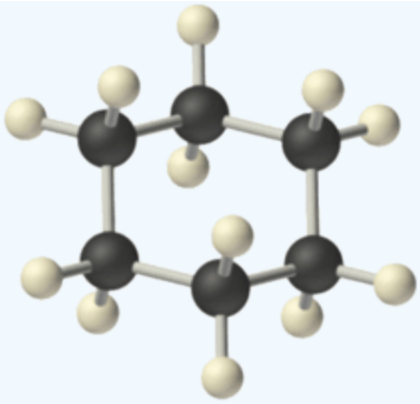
Strategy: Assess the relative magnitude of the enthalpy change for each step in the process shown in Figure 13.1.2. Then use Table 13.1.2 to predict the solubility of each compound in water and arrange them in order of decreasing solubility.

Solution:

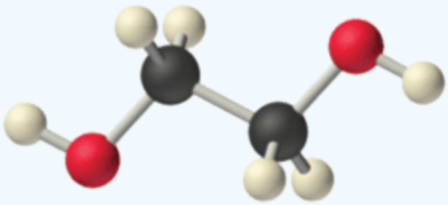
The first substance, LiCl, is an ionic compound, so a great deal of energy is required to separate its anions and cations and overcome the lattice energy (ΔH_2 is far greater than zero in Equation 13.1.1). Because water is a polar substance, the interactions between both Li^+ and Cl^- ions and water should be favorable and strong. Thus we expect ΔH_3 to be far less than zero, making LiCl soluble in water. In contrast, naphthalene is a nonpolar compound, with only London dispersion forces holding the molecules together in the solid state. We therefore expect ΔH_2 to be small and positive. We also expect the interaction between polar water molecules and nonpolar naphthalene molecules to be weak $\Delta H_3 \approx 0$. Hence we do not expect naphthalene to be very soluble in water, if at all. Benzoic acid has a polar carboxylic acid group and a nonpolar aromatic ring. We therefore expect that the energy required to separate solute molecules (ΔH_2) will be greater than for naphthalene and less than for LiCl. The strength of the interaction of benzoic acid with water should also be intermediate between those of LiCl and naphthalene. Hence benzoic acid is expected to be more soluble in water than naphthalene but less soluble than LiCl. We thus predict LiCl to be the most soluble in water and naphthalene to be the least soluble.

Exercise 13.1.1

Considering ammonium chloride, cyclohexane, and ethylene glycol ($HOCH_2CH_2OH$), which will be most soluble and which will be least soluble in benzene?



Cyclohexane



Ethylene glycol

Answer available at the end of this section.

Summary

Solutions are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the solvent, and the components present in lesser amounts are the solute(s). The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are miscible, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are immiscible. Solvation is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called hydration. The overall enthalpy change that accompanies the formation of a solution, ΔH_{soln}, is the sum of the enthalpy change for breaking the intermolecular interactions in both the solvent and the solute and the enthalpy change for the formation of new solute–solvent interactions. Exothermic ($\Delta H_{soln} < 0$) processes favor solution formation. In addition, the change in entropy, the degree of disorder of the system, must be considered when predicting whether a solution will form. An increase in entropy (a decrease in order) favors dissolution.

Answers

Exercise 13.1.1

The most soluble is cyclohexane; the least soluble is ammonium chloride.

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13.2: Saturated Solutions and Solubility

Learning Objectives

- To understand the relationship between solubility and molecular structure.
- To demonstrate how the strength of intramolecular bonding determines the solubility of a solute in a given solvent.

When a solute dissolves, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution (Figure $13.2.1a$). This is not, however, a unidirectional process. If the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called crystallization. Dissolution and crystallization continue as long as excess solid is present, resulting in a dynamic equilibrium analogous to the equilibrium that maintains the vapor pressure of a liquid. We can represent these opposing processes as follows:

$$solute + solvent \underset{crystallization}{\overset{dissolution}{\longrightleftharpoons}} solution$$

Although the terms precipitation and crystallization are both used to describe the separation of solid solute from a solution, crystallization refers to the formation of a solid with a well-defined crystalline structure, whereas precipitation refers to the formation of any solid phase, often one with very small particles.

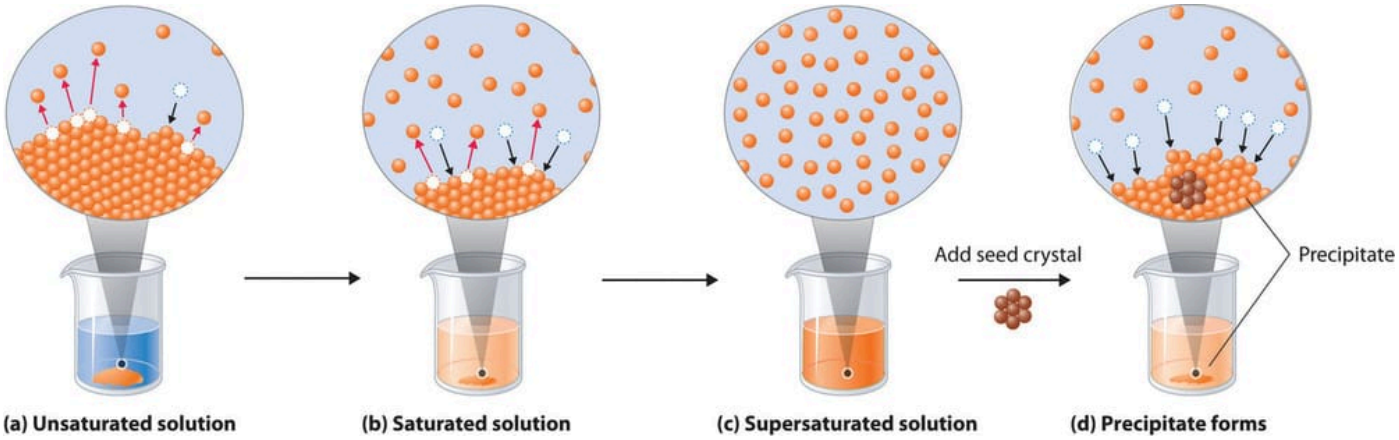


Figure $13.2.1$: Dissolution and Precipitation. (a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.

Starting on the left the solution starts are unsaturated, then saturated, then supersaturated, when seed crystal is added a precipitate forms.

Factors Affecting Solubility

The maximum amount of a solute that can dissolve in a solvent at a specified temperature and pressure is its solubility. Solubility is often expressed as the mass of solute per volume (g/L) or mass of solute per mass of solvent (g/g), or as the moles of solute per volume (mol/L). Even for very soluble substances, however, there is usually a limit to how much solute can dissolve in a given quantity of solvent. In general, the solubility of a substance depends on not only the energetic factors we have discussed but also the temperature and, for gases, the pressure. At 20°C, for example, 177 g of NaI, 91.2 g of NaBr, 35.9 g of NaCl, and only 4.1 g of NaF dissolve in 100 g of water. At 70°C, however, the solubilities increase to 295 g of NaI, 119 g of NaBr, 37.5 g of NaCl, and 4.8 g of NaF. As you learned in Chapter 12, the lattice energies of the sodium halides increase from NaI to NaF. The fact that the solubilities decrease as the lattice energy increases suggests that the ΔH_2 term in Figure 13.1 dominates for this series of compounds.

A solution with the maximum possible amount of solute is saturated. If a solution contains less than the maximum amount of solute, it is unsaturated. When a solution is saturated and excess solute is present, the rate of dissolution is exactly equal to the rate of crystallization (Figure $13.2.1b$). Using the value just stated, a saturated aqueous solution of NaCl, for example, contains 35.9 g of NaCl per 100 mL of water at 20°C. We can prepare a homogeneous saturated solution by adding excess solute (in this case, greater than 35.9 g of NaCl) to the solvent (water), stirring until the maximum possible amount of solute has dissolved, and then removing undissolved solute by filtration.

The solubility of most solids increases with increasing temperature.

Because the solubility of most solids increases with increasing temperature, a saturated solution that was prepared at a higher temperature usually contains more dissolved solute than it would contain at a lower temperature. When the solution is cooled, it can therefore become supersaturated (Figure $13.2.1c$). Like a supercooled or superheated liquid, a supersaturated solution is unstable. Consequently, adding a small particle of the solute, a seed crystal, will usually cause the excess solute to rapidly precipitate or crystallize, sometimes with spectacular results. The rate of crystallization in Equation $???$ is greater than the rate of dissolution, so crystals or a precipitate form (Figure $13.2.1d$). In contrast, adding a seed crystal to a saturated solution reestablishes the dynamic equilibrium, and the net quantity of dissolved solute no longer changes.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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Video $13.2.1$***:*** *hot ice (sodium acetate) beautiful science experiment. watered-down sodium acetate trihydrate. Needle crystal is truly wonderful structures*

Because crystallization is the reverse of dissolution, a substance that requires an input of heat to form a solution ($\Delta H_{soln} > 0$) releases that heat when it crystallizes from solution ($\Delta H_{crys} < 0$). The amount of heat released is proportional to the amount of solute that exceeds its solubility. Two substances that have a positive enthalpy of solution are sodium thiosulfate ($Na_2S_2O_3$) and sodium acetate (CH_3CO_2Na), both of which are used in commercial hot packs, small bags of supersaturated solutions used to warm hands (see Figure 13.1.3).

Interactions in Liquid Solutions

The interactions that determine the solubility of a substance in a liquid depend largely on the chemical nature of the solute (such as whether it is ionic or molecular) rather than on its physical state (solid, liquid, or gas). We will first describe the general case of forming a solution of a molecular species in a liquid solvent and then describe the formation of a solution of an ionic compound.

Solutions of Molecular Substances in Liquids

The London dispersion forces, dipole–dipole interactions, and hydrogen bonds that hold molecules to other molecules are generally weak. Even so, energy is required to disrupt these interactions. As described in Section 13.1, unless some of that energy is recovered in the formation of new, favorable solute–solvent interactions, the increase in entropy on solution formation is not enough for a solution to form.

For solutions of gases in liquids, we can safely ignore the energy required to separate the solute molecules ($\Delta H_2 = 0$) because the molecules are already separated. Thus we need to consider only the energy required to separate the solvent molecules (ΔH_1) and the energy released by new solute–solvent interactions (ΔH_3). Nonpolar gases such as N_2, O_2, and Ar have no dipole moment and cannot engage in dipole–dipole interactions or hydrogen bonding. Consequently, the only way they can interact with a solvent is by means of London dispersion forces, which may be weaker than the solvent–solvent interactions in a polar solvent. It is not surprising, then, that nonpolar gases are most soluble in nonpolar solvents. In this case, ΔH_1 and ΔH_3 are both small and of similar magnitude. In contrast, for a solution of a nonpolar gas in a polar solvent, ΔH_1 is far greater than ΔH_3. As a result,

nonpolar gases are less soluble in polar solvents than in nonpolar solvents. For example, the concentration of N_2 in a saturated solution of N_2 in water, a polar solvent, is only $7.07 \times 10^{-4}\ M$ compared with $4.5 \times 10^{-3}\ M$ for a saturated solution of N_2 in benzene, a nonpolar solvent.

The solubilities of nonpolar gases in water generally increase as the molecular mass of the gas increases, as shown in Table 13.2.1. This is precisely the trend expected: as the gas molecules become larger, the strength of the solvent–solute interactions due to London dispersion forces increases, approaching the strength of the solvent–solvent interactions.

Table 13.2.1: Solubilities of Selected Gases in Water at 20°C and 1 atm Pressure

Gas	Solubility (M) × 10^{-4}
He	3.90
Ne	4.65
Ar	15.2
Kr	27.9
Xe	50.2
H_2	8.06
N_2	7.07
CO	10.6
O2	13.9
N_2O	281
CH_4	15.5

Virtually all common organic liquids, whether polar or not, are miscible. The strengths of the intermolecular attractions are comparable; thus the enthalpy of solution is expected to be small ($\Delta H_{soln} \approx 0$), and the increase in entropy drives the formation of a solution. If the predominant intermolecular interactions in two liquids are very different from one another, however, they may be immiscible. For example, organic liquids such as benzene, hexane, CCl_4, and CS_2 (S=C=S) are nonpolar and have no ability to act as hydrogen bond donors or acceptors with hydrogen-bonding solvents such as H_2O, HF, and NH_3; hence they are immiscible in these solvents. When shaken with water, they form separate phases or layers separated by an interface (Figure 13.2.2), the region between the two layers.

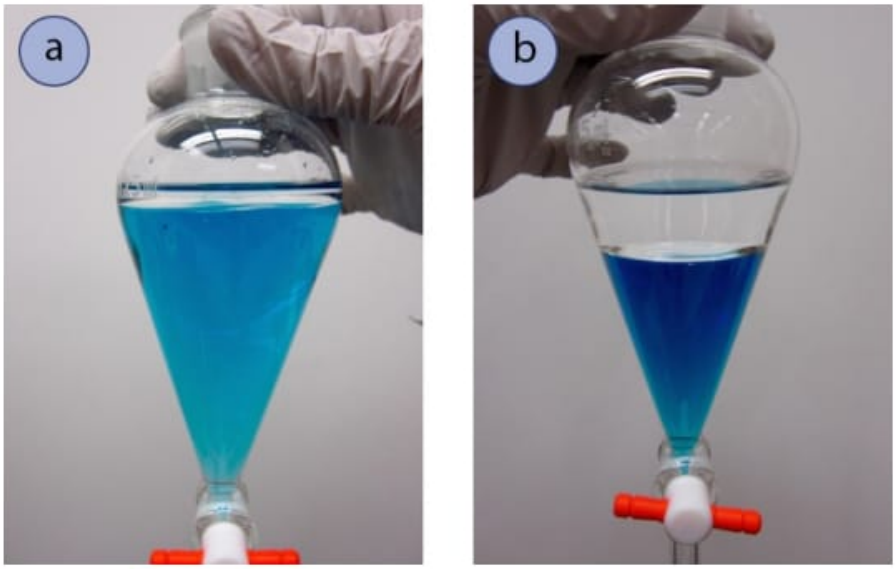


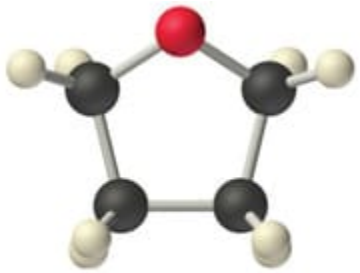
Figure 13.2.2: Immiscible Liquids. Separatory funnel demonstrating the separation of oil and colored water. 10 mL organic solvent (hexanes) with 100 mL water (colored with blue dye) in a 125 mL separatory funnel, b) 40 mL each of organic solvent (ethyl acetate), and water (colored with blue dye). from Lisa Nichols (CC-BY-SA-ND).

Just because two liquids are immiscible, however, does not mean that they are completely insoluble in each other. For example, 188 mg of benzene dissolves in 100 mL of water at 23.5°C. Adding more benzene results in the separation of an upper layer consisting of benzene with a small amount of dissolved water (the solubility of water in benzene is only 178 mg/100 mL of benzene). The solubilities of simple alcohols in water are given in Table 13.2.2.

Table 13.2.2: Solubilities of Straight-Chain Organic Alcohols in Water at 20°C

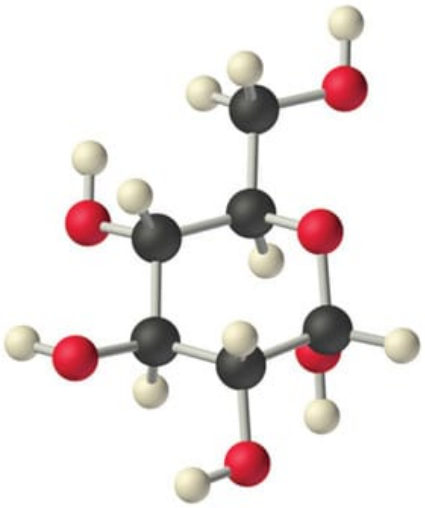
Alcohol	Solubility (mol/100 g of H_2O)
methanol	completely miscible
ethanol	completely miscible
n-propanol	completely miscible
n-butanol	0.11
n-pentanol	0.030
n-hexanol	0.0058
n-heptanol	0.0008

Only the three lightest alcohols (methanol, ethanol, and n-propanol) are completely miscible with water. As the molecular mass of the alcohol increases, so does the proportion of hydrocarbon in the molecule. Correspondingly, the importance of hydrogen bonding and dipole–dipole interactions in the pure alcohol decreases, while the importance of London dispersion forces increases, which leads to progressively fewer favorable electrostatic interactions with water. Organic liquids such as acetone, ethanol, and tetrahydrofuran are sufficiently polar to be completely miscible with water yet sufficiently nonpolar to be completely miscible with all organic solvents.



Tetrahydrofuran (THF)

The same principles govern the solubilities of molecular solids in liquids. For example, elemental sulfur is a solid consisting of cyclic S_8 molecules that have no dipole moment. Because the S_8 rings in solid sulfur are held to other rings by London dispersion forces, elemental sulfur is insoluble in water. It is, however, soluble in nonpolar solvents that have comparable London dispersion forces, such as CS_2 (23 g/100 mL). In contrast, glucose contains five –OH groups that can form hydrogen bonds. Consequently, glucose is very soluble in water (91 g/120 mL of water) but essentially insoluble in nonpolar solvents such as benzene. The structure of one isomer of glucose is shown here.



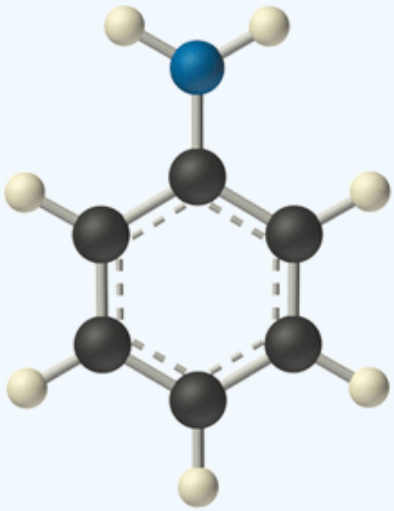
D-Glucose

Low-molecular-mass hydrocarbons with highly electronegative and polarizable halogen atoms, such as chloroform ($CHCl_3$) and methylene chloride (CH_2Cl_2), have both significant dipole moments and relatively strong London dispersion forces. These hydrocarbons are therefore powerful solvents for a wide range of polar and nonpolar compounds. Naphthalene, which is nonpolar, and phenol (C_6H_5OH), which is polar, are very soluble in chloroform. In contrast, the solubility of ionic compounds is largely determined not by the polarity of the solvent but rather by its dielectric constant, a measure of its ability to separate ions in solution, as you will soon see.

Example 13.2.1

Identify the most important solute–solvent interactions in each solution.

a. iodine in benzene solvent
b. aniline ($\mathrm{C_6H_5NH_2}$) in dichloromethane ($\mathrm{CH_2Cl_2}$) solvent



Aniline

c. iodine in water solvent

Given: components of solutions

Asked for: predominant solute–solvent interactions

Strategy:

Identify all possible intermolecular interactions for both the solute and the solvent: London dispersion forces, dipole–dipole interactions, or hydrogen bonding. Determine which is likely to be the most important factor in solution formation.

Solution

a. Benzene and $\mathrm{I_2}$ are both nonpolar molecules. The only possible attractive forces are London dispersion forces.
b. Aniline is a polar molecule with a dipole moment of 1.6 D and has an $-\mathrm{NH_2}$ group that can act as a hydrogen bond donor. Dichloromethane is also polar with a 1.5 D dipole moment, but it has no obvious hydrogen bond acceptor. Therefore, the most important interactions between aniline and CH_2Cl_2 are likely to be dipole-dipole interactions.
c. Water is a highly polar molecule that engages in extensive hydrogen bonding, whereas I_2 is a nonpolar molecule that cannot act as a hydrogen bond donor or acceptor. The slight solubility of $\mathrm{I_2}$ in water ($1.3 \times 10^{-3}\ mol/L$ at 25°C) is due to London dispersion forces.

Exercise 13.2.1

Identify the most important interactions in each solution:

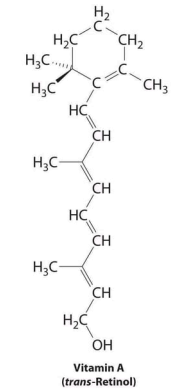
a. ethylene glycol ($HOCH_2CH_2OH$) in acetone
b. acetonitrile ($\mathrm{CH_3C{\equiv}N}$) in acetone
c. n-hexane in benzene

Answer a available at the end of this section.

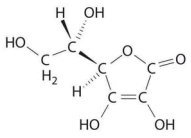
Hydrophilic and Hydrophobic Solutes

A solute can be classified as hydrophilic (literally, “water loving”), meaning that it has an electrostatic attraction to water, or hydrophobic (“water fearing”), meaning that it repels water. A hydrophilic substance is polar and often contains O–H or N–H groups that can form hydrogen bonds to water. For example, glucose with its five O–H groups is hydrophilic. In contrast, a hydrophobic substance may be polar but usually contains C–H bonds that do not interact favorably with water, as is the case with naphthalene and n-octane. Hydrophilic substances tend to be very soluble in water and other strongly polar solvents, whereas hydrophobic substances are essentially insoluble in water and soluble in nonpolar solvents such as benzene and cyclohexane.

The difference between hydrophilic and hydrophobic substances has substantial consequences in biological systems. For example, vitamins can be classified as either fat soluble or water soluble. Fat-soluble vitamins, such as vitamin A, are mostly nonpolar, hydrophobic molecules. As a result, they tend to be absorbed into fatty tissues and stored there. In contrast, water-soluble vitamins, such as vitamin C, are polar, hydrophilic molecules that circulate in the blood and intracellular fluids, which are primarily aqueous. Water-soluble vitamins are therefore excreted much more rapidly from the body and must be replenished in our daily diet. A comparison of the chemical structures of vitamin A and vitamin C quickly reveals why one is hydrophobic and the other hydrophilic.



Vitamin A
(*trans*-Retinol)

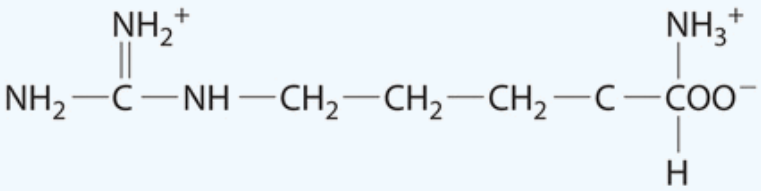


Vitamin C
(L-Ascorbic acid)

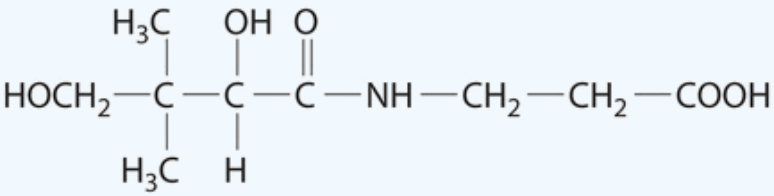
Because water-soluble vitamins are rapidly excreted, the risk of consuming them in excess is relatively small. Eating a dozen oranges a day is likely to make you tired of oranges long before you suffer any ill effects due to their high vitamin C content. In contrast, fat-soluble vitamins constitute a significant health hazard when consumed in large amounts. For example, the livers of polar bears and other large animals that live in cold climates contain large amounts of vitamin A, which have occasionally proven fatal to humans who have eaten them.

Example 13.2.2

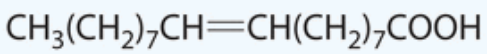
The following substances are essential components of the human diet:



Arginine



Pantothenic acid



Oleic acid

Using what you know of hydrophilic and hydrophobic solutes, classify each as water soluble or fat soluble and predict which are likely to be required in the diet on a daily basis.

a. arginine
b. pantothenic acid
c. oleic acid

Given: chemical structures

Asked for: classification as water soluble or fat soluble; dietary requirement

Strategy:

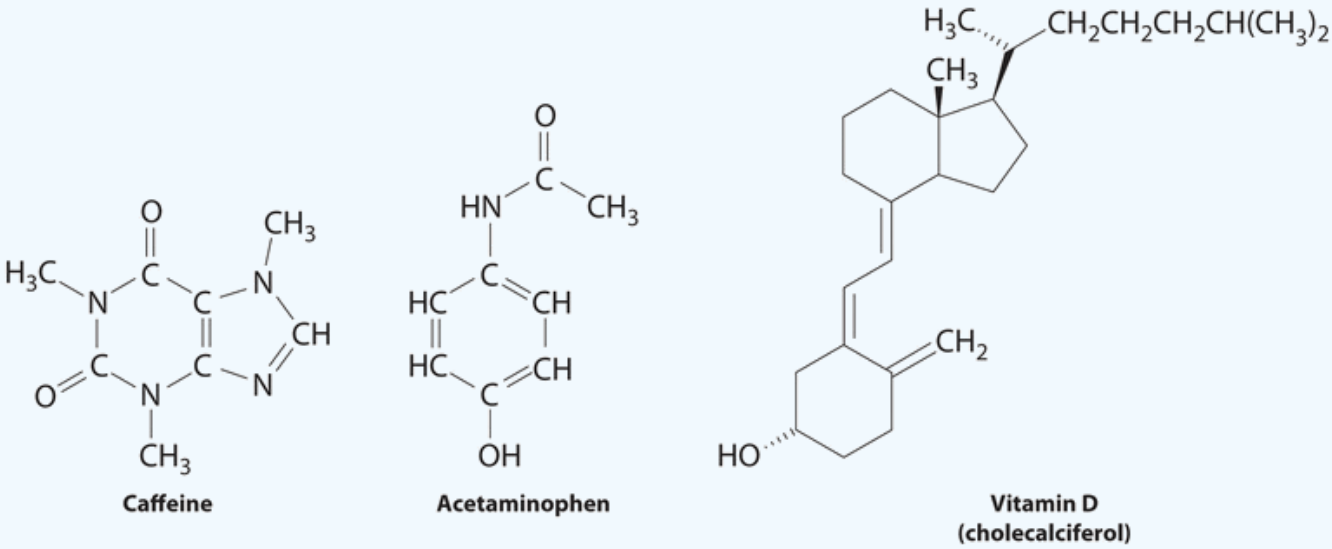
Based on the structure of each compound, decide whether it is hydrophilic or hydrophobic. If it is hydrophilic, it is likely to be required on a daily basis.

Solution:

a. Arginine is a highly polar molecule with two positively charged groups and one negatively charged group, all of which can form hydrogen bonds with water. As a result, it is hydrophilic and required in our daily diet.
b. Although pantothenic acid contains a hydrophobic hydrocarbon portion, it also contains several polar functional groups ($-\mathrm{OH}$ and $-\mathrm{CO_2H}$) that should interact strongly with water. It is therefore likely to be water soluble and required in the diet. (In fact, pantothenic acid is almost always a component of multiple-vitamin tablets.)
c. Oleic acid is a hydrophobic molecule with a single polar group at one end. It should be fat soluble and not required daily.

Exercise 13.2.2

These compounds are consumed by humans: caffeine, acetaminophen, and vitamin D. Identify each as primarily hydrophilic (water soluble) or hydrophobic (fat soluble), and predict whether each is likely to be excreted from the body rapidly or slowly.



Answer available at the end of this section.

Solid Solutions

Solutions are not limited to gases and liquids; solid solutions also exist. For example, amalgams, which are usually solids, are solutions of metals in liquid mercury. Because most metals are soluble in mercury, amalgams are used in gold mining, dentistry, and many other applications. A major difficulty when mining gold is separating very small particles of pure gold from tons of crushed rock. One way to accomplish this is to agitate a suspension of the crushed rock with liquid mercury, which dissolves the gold (as well as any metallic silver that might be present). The very dense liquid gold–mercury amalgam is then isolated and the mercury distilled away.

An alloy is a solid or liquid solution that consists of one or more elements in a metallic matrix. A solid alloy has a single homogeneous phase in which the crystal structure of the solvent remains unchanged by the presence of the solute. Thus the microstructure of the alloy is uniform throughout the sample. Examples are substitutional and interstitial alloys such as brass or solder. Liquid alloys include sodium/potassium and gold/mercury. In contrast, a partial alloy solution has two or more phases that

can be homogeneous in the distribution of the components, but the microstructures of the two phases are not the same. As a liquid solution of lead and tin is cooled, for example, different crystalline phases form at different cooling temperatures. Alloys usually have properties that differ from those of the component elements.

Network solids such as diamond, graphite, and $\mathrm{SiO_2}$ are insoluble in all solvents with which they do not react chemically. The covalent bonds that hold the network or lattice together are simply too strong to be broken under normal conditions. They are certainly much stronger than any conceivable combination of intermolecular interactions that might occur in solution. Most metals are insoluble in virtually all solvents for the same reason: the delocalized metallic bonding is much stronger than any favorable metal atom–solvent interactions. Many metals react with solutions such as aqueous acids or bases to produce a solution. However, as we saw in Section 13.1, in these instances the metal undergoes a chemical transformation that cannot be reversed by simply removing the solvent.

Solids with very strong intermolecular bonding tend to be insoluble.

Solubilities of Ionic Substances in Liquids

Previously, you were introduced to guidelines for predicting the solubility of ionic compounds in water. Ionic substances are generally most soluble in polar solvents; the higher the lattice energy, the more polar the solvent must be to overcome the lattice energy and dissolve the substance. Because of its high polarity, water is the most common solvent for ionic compounds. Many ionic compounds are soluble in other polar solvents, however, such as liquid ammonia, liquid hydrogen fluoride, and methanol. Because all these solvents consist of molecules that have relatively large dipole moments, they can interact favorably with the dissolved ions.

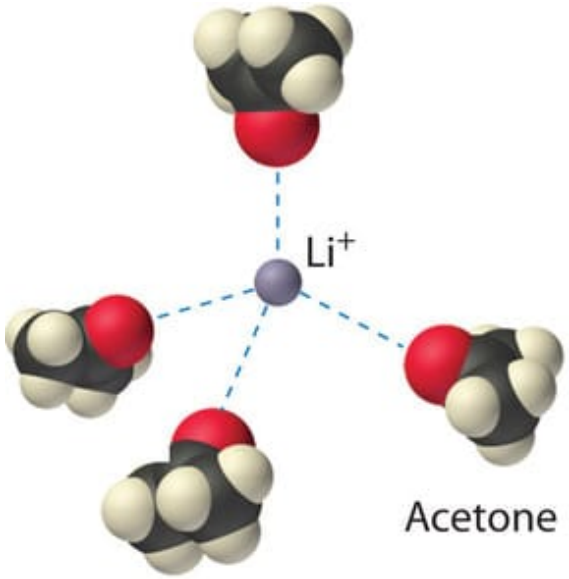


Figure $13.2.3$: Ion–Dipole Interactions in the Solvation of $\mathrm{Li^+}$ Ions by Acetone, a Polar Solvent

The ion–dipole interactions between $\mathrm{Li^+}$ ions and acetone molecules in a solution of LiCl in acetone are shown in Figure $13.2.3$. The energetically favorable $\mathrm{Li^+}$–acetone interactions make ΔH_3 sufficiently negative to overcome the positive ΔH_1 and ΔH_2. Because the dipole moment of acetone (2.88 D), and thus its polarity, is actually larger than that of water (1.85 D), one might even expect that LiCl would be more soluble in acetone than in water. In fact, the opposite is true: 83 g of LiCl dissolve in 100 mL of water at 20°C, but only about 4.1 g of LiCl dissolve in 100 mL of acetone. This apparent contradiction arises from the fact that the dipole moment is a property of a single molecule in the gas phase. A more useful measure of the ability of a solvent to dissolve ionic compounds is its **dielectric constant** (ε), which is the ability of a bulk substance to decrease the electrostatic forces between two charged particles. By definition, the dielectric constant of a vacuum is 1. In essence, a solvent with a high dielectric constant causes the charged particles to behave as if they have been moved farther apart. At 25°C, the dielectric constant of water is 80.1, one of the highest known, and that of acetone is only 21.0. Hence water is better able to decrease the electrostatic attraction between $\mathrm{Li^+}$ and $\mathrm{Cl^-}$ ions, so LiCl is more soluble in water than in acetone. This behavior is in contrast to that of molecular substances, for which polarity is the dominant factor governing solubility.

A solvent's dielectric constant is the most useful measure of its ability to dissolve ionic compounds. A solvent's polarity

is the dominant factor in dissolving molecular substances.

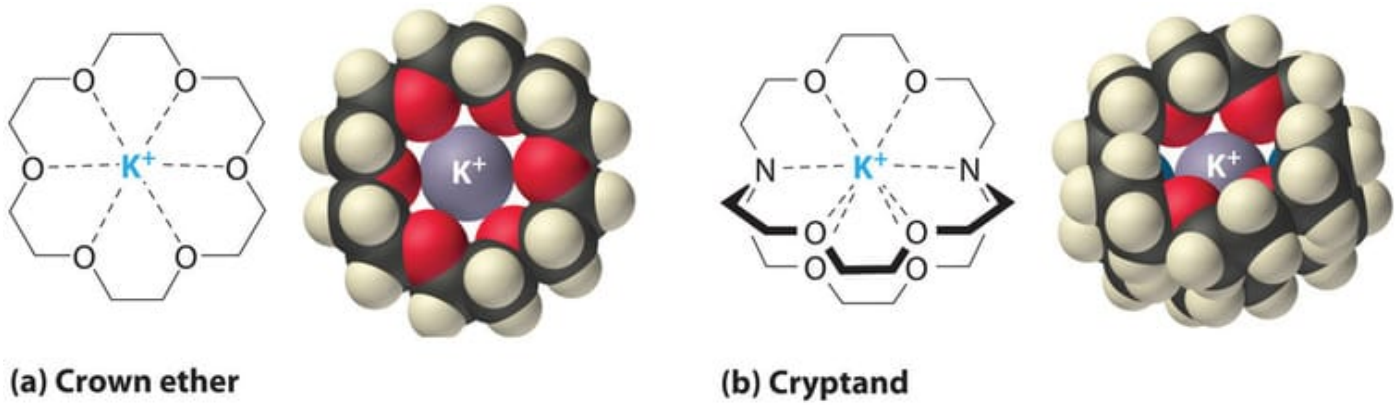


Figure 13.2.4: Crown Ethers and Cryptands. (a) The potassium complex of the crown ether 18-crown-6. Note how the cation is nestled within the central cavity of the molecule and interacts with lone pairs of electrons on the oxygen atoms. (b) The potassium complex of 2,2,2-cryptand, showing how the cation is almost hidden by the cryptand. Cryptands solvate cations via lone pairs of electrons on both oxygen and nitrogen atoms.

It is also possible to dissolve ionic compounds in organic solvents using crown ethers, cyclic compounds with the general formula $(OCH_2CH_2)_n$. Crown ethers are named using both the total number of atoms in the ring and the number of oxygen atoms. Thus 18-crown-6 is an 18-membered ring with six oxygen atoms (Figure 13.2.1*a*). The cavity in the center of the crown ether molecule is lined with oxygen atoms and is large enough to be occupied by a cation, such as K^+. The cation is stabilized by interacting with lone pairs of electrons on the surrounding oxygen atoms. Thus crown ethers solvate cations inside a hydrophilic cavity, whereas the outer shell, consisting of C–H bonds, is hydrophobic. Crown ethers are useful for dissolving ionic substances such as $KMnO_4$ in organic solvents such as isopropanol $[(CH_3)_2CHOH]$ (Figure 13.2.5). The availability of crown ethers with cavities of different sizes allows specific cations to be solvated with a high degree of selectivity.

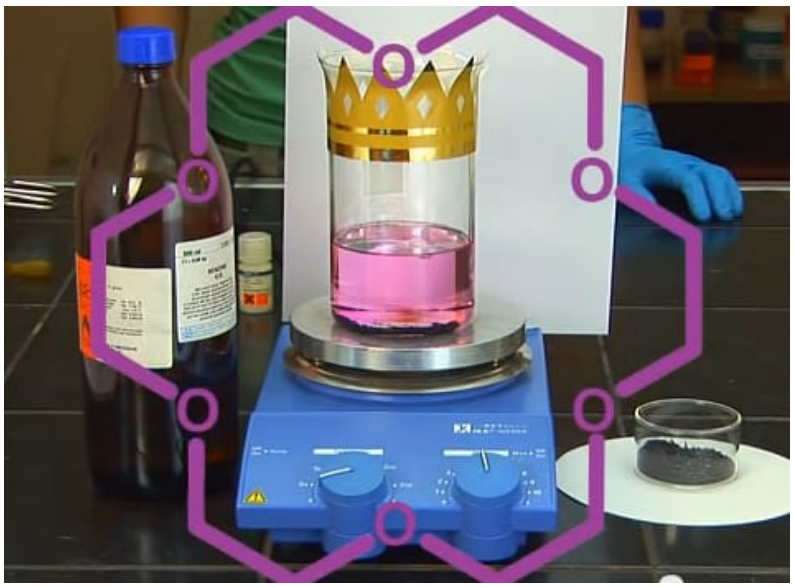


Figure 13.2.5: Potassium permanganate is insoluble in benzene. However, upon addition of crown ether soluble colored complex is formed. (left) Normally $KMnO_4$, which is intensely purple, is completely insoluble in isopropanol, which has a relatively low dielectric constant. (right) In the presence of a small amount of 18-crown-6, $KMnO_4$ dissolves in benzene, as shown by the reddish-purple color caused by permanganate ions in solution. Full video can be found here: www.youtube.com/watch?v=JsowvWBvz74.

Cryptands (from the Greek kryptós, meaning “hidden”) are compounds that can completely surround a cation with lone pairs of electrons on oxygen and nitrogen atoms (Figure 13.2.4*b*). The number in the name of the cryptand is the number of oxygen atoms in each strand of the molecule. Like crown ethers, cryptands can be used to prepare solutions of ionic compounds in solvents that are otherwise too nonpolar to dissolve them.

Summary

The solubility of a substance is the maximum amount of a solute that can dissolve in a given quantity of solvent; it depends on the chemical nature of both the solute and the solvent and on the temperature and pressure. When a solution contains the maximum amount of solute that can dissolve under a given set of conditions, it is a saturated solution. Otherwise, it is unsaturated. Supersaturated solutions, which contain more dissolved solute than allowed under particular conditions, are not stable; the addition of a seed crystal, a small particle of solute, will usually cause the excess solute to crystallize. A system in which crystallization and dissolution occur at the same rate is in dynamic equilibrium. The solubility of a substance in a liquid is determined by intermolecular interactions, which also determine whether two liquids are miscible. Solutes can be classified as hydrophilic (water loving) or hydrophobic (water fearing). Vitamins with hydrophilic structures are water soluble, whereas those with hydrophobic structures are fat soluble. Many metals dissolve in liquid mercury to form amalgams. Covalent network solids and most metals are insoluble in nearly all solvents. The solubility of ionic compounds is largely determined by the dielectric constant (ε) of the solvent, a measure of its ability to decrease the electrostatic forces between charged particles. Solutions of many ionic compounds in organic solvents can be dissolved using crown ethers, cyclic polyethers large enough to accommodate a metal ion in the center, or cryptands, compounds that completely surround a cation.

Answers

Exercise 13.2.1

hydrogen bonding

London interactions

London dispersion forces

Exercise 13.2.2

Caffeine and acetaminophen are water soluble and rapidly excreted, whereas vitamin D is fat soluble and slowly excreted

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13.3: Factors Affecting Solubility

Learning Objectives

- To understand the relationship among temperature, pressure, and solubility.
- The understand that the solubility of a solid may increase or decrease with increasing temperature,
- To understand that the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

Experimentally it is found that the solubility of most compounds depends strongly on temperature and, if a gas, on pressure as well. As we shall see, the ability to manipulate the solubility by changing the temperature and pressure has several important consequences.

Effect of Temperature on the Solubility of Solids

Figure $13.3.1$ shows plots of the solubilities of several organic and inorganic compounds in water as a function of temperature. Although the solubility of a solid generally increases with increasing temperature, there is no simple relationship between the structure of a substance and the temperature dependence of its solubility. Many compounds (such as glucose and $\mathrm{CH_3CO_2Na}$) exhibit a dramatic increase in solubility with increasing temperature. Others (such as NaCl and $\mathrm{K_2SO_4}$) exhibit little variation, and still others (such as $\mathrm{Li_2SO_4}$) become less soluble with increasing temperature.

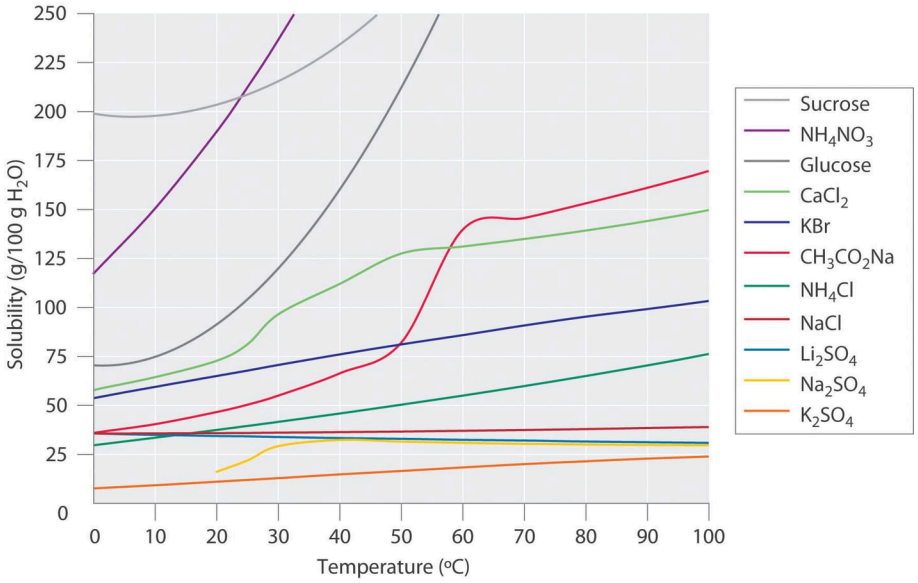


Figure $13.3.1$: Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds. (CC BY-SA-NC; anonymous)

Graph of solubility against temperature. Plots of sucrose, NH4NO3, glucose, CaCl2, KBr, CH3CO2Na, NH4Cl, Li2SO4, Na2SO4, K2SO4.

Notice in particular the curves for $\mathrm{NH_4NO_3}$ and $\mathrm{CaCl_2}$. The dissolution of ammonium nitrate in water is endothermic ($\Delta H_{soln} = +25.7\ kJ/mol$), whereas the dissolution of calcium chloride is exothermic ($\Delta H_{soln} = -68.2\ kJ/mol$), yet Figure $13.3.1$ shows that the solubility of both compounds increases sharply with increasing temperature. In fact, the magnitudes of the changes in both enthalpy and entropy for dissolution are temperature dependent. Because the solubility of a compound is ultimately determined by relatively small differences between large numbers, there is generally no good way to predict how the solubility will vary with temperature.

The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by fractional crystallization, the separation of compounds on the basis of their solubilities in a given solvent. For example, if we have

a mixture of 150 g of sodium acetate (CH_3CO_2Na) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C. According to the temperature curves in Figure 13.3.1, both compounds dissolve in water at 80°C, and all 50 g of KBr remains in solution at 0°C. Only about 36 g of CH_3CO_2Na are soluble in 100 g of water at 0°C, however, so approximately 114 g (150 g – 36 g) of CH_3CO_2Na crystallizes out on cooling. The crystals can then be separated by filtration. Thus fractional crystallization allows us to recover about 75% of the original CH_3CO_2Na in essentially pure form in only one step.

Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure 13.3.1 and from antibiotics to enzymes. For the technique to work properly, the compound of interest must be more soluble at high temperature than at low temperature, so that lowering the temperature causes it to crystallize out of solution. In addition, the impurities must be more soluble than the compound of interest (as was KBr in this example) and preferably present in relatively small amounts.

Effect of Temperature on the Solubility of Gases

The solubility of gases in liquids decreases with increasing temperature, as shown in Figure 13.3.2. Attractive intermolecular interactions in the gas phase are essentially zero for most substances. When a gas dissolves, it does so because its molecules interact with solvent molecules. Because heat is released when these new attractive interactions form, dissolving most gases in liquids is an exothermic process ($\Delta H_{soln} < 0$). Conversely, adding heat to the solution provides thermal energy that overcomes the attractive forces between the gas and the solvent molecules, thereby decreasing the solubility of the gas. The phenomenon is similar to that involved in the increase in the vapor pressure of a pure liquid with increasing temperature. In the case of vapor pressure, however, it is attractive forces between solvent molecules that are being overcome by the added thermal energy when the temperature is increased.

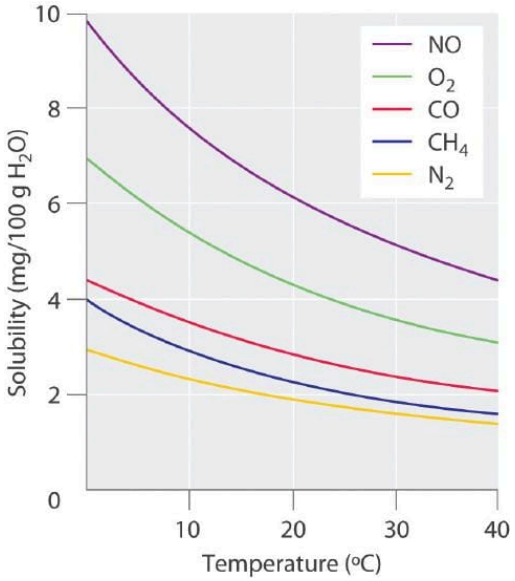


Figure 13.3.2: Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm. The solubilities of all gases decrease with increasing temperature. (CC BY-SA-NC; anonymous)

The decrease in the solubilities of gases at higher temperatures has both practical and environmental implications. Anyone who routinely boils water in a teapot or electric kettle knows that a white or gray deposit builds up on the inside and must eventually be removed. The same phenomenon occurs on a much larger scale in the giant boilers used to supply hot water or steam for industrial applications, where it is called “boiler scale,” a deposit that can seriously decrease the capacity of hot water pipes (Figure 13.3.3). The problem is not a uniquely modern one: aqueducts that were built by the Romans 2000 years ago to carry cold water from alpine regions to warmer, drier regions in southern France were clogged by similar deposits. The chemistry behind the formation of these deposits is moderately complex and will be described elsewhere, but the driving force is the loss of dissolved CO_2 from solution. Hard water contains dissolved Ca^{2+} and HCO_3^- (bicarbonate) ions. Calcium bicarbonate ($Ca(HCO_3)_2$ is rather soluble in water, but calcium carbonate ($CaCO_3$) is quite insoluble. A solution of bicarbonate ions can react to form carbon dioxide, carbonate ion, and water:

$$2\,HCO_3^-\,(aq) \longrightarrow CO_3^{2-}\,(aq) + H_2O\,(l) + CO_2\,(aq) \tag{13.3.1}$$

Heating the solution decreases the solubility of $\mathrm{CO_2}$, which escapes into the gas phase above the solution. In the presence of calcium ions, the carbonate ions precipitate as insoluble calcium carbonate, the major component of boiler scale.



Figure 13.3.3: Calcium carbonate deposits (left) Calcium carbonate ($CaCO_3$) deposits in hot water pipes can significantly reduce pipe capacity. These deposits, called boiler scale, form when dissolved $\mathrm{CO_2}$ is driven into the gas phase at high temperatures. (right) Highly calcified remains of Eiffel aqueduct near Euskirchen-Kreuzweingarten, Germany. (Wikipedia)

Thermal Pollution

In **thermal pollution**, lake or river water that is used to cool an industrial reactor or a power plant is returned to the environment at a higher temperature than normal. Because of the reduced solubility of $\mathrm{O_2}$ at higher temperatures (Figure 13.3.2), the warmer water contains less dissolved oxygen than the water did when it entered the plant. Fish and other aquatic organisms that need dissolved oxygen to live can literally suffocate if the oxygen concentration of their habitat is too low. Because the warm, oxygen-depleted water is less dense, it tends to float on top of the cooler, denser, more oxygen-rich water in the lake or river, forming a barrier that prevents atmospheric oxygen from dissolving. Eventually even deep lakes can be suffocated if the problem is not corrected. Additionally, most fish and other nonmammalian aquatic organisms are cold-blooded, which means that their body temperature is the same as the temperature of their environment. Temperatures substantially greater than the normal range can lead to severe stress or even death. Cooling systems for power plants and other facilities must be designed to minimize any adverse effects on the temperatures of surrounding bodies of water.



There are many causes of fish kill, but oxygen depletion is the most common cause. (Public Domain; United States Fish and Wildlife Service)

A similar effect is seen in the rising temperatures of bodies of water such as the k0oi89Chesapeake Bay, the largest estuary in North America, where \lobal warming has been implicated as the cause. For each 1.5°C that the bay's water warms, the capacity of water to dissolve oxygen decreases by about 1.1%. Many marine species that are at the southern limit of their distributions have shifted their populations farther north. In 2005, the eelgrass, which forms an important nursery habitat for fish and shellfish, disappeared from much of the bay following record high water temperatures. Presumably, decreased oxygen levels decreased populations of clams and other filter feeders, which then decreased light transmission to allow the eelsgrass to grow. The complex relationships in ecosystems such as the Chesapeake Bay are especially sensitive to temperature fluctuations that cause a deterioration of habitat quality.

Effect of Pressure on the Solubility of Gases: Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 13.3.4, which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

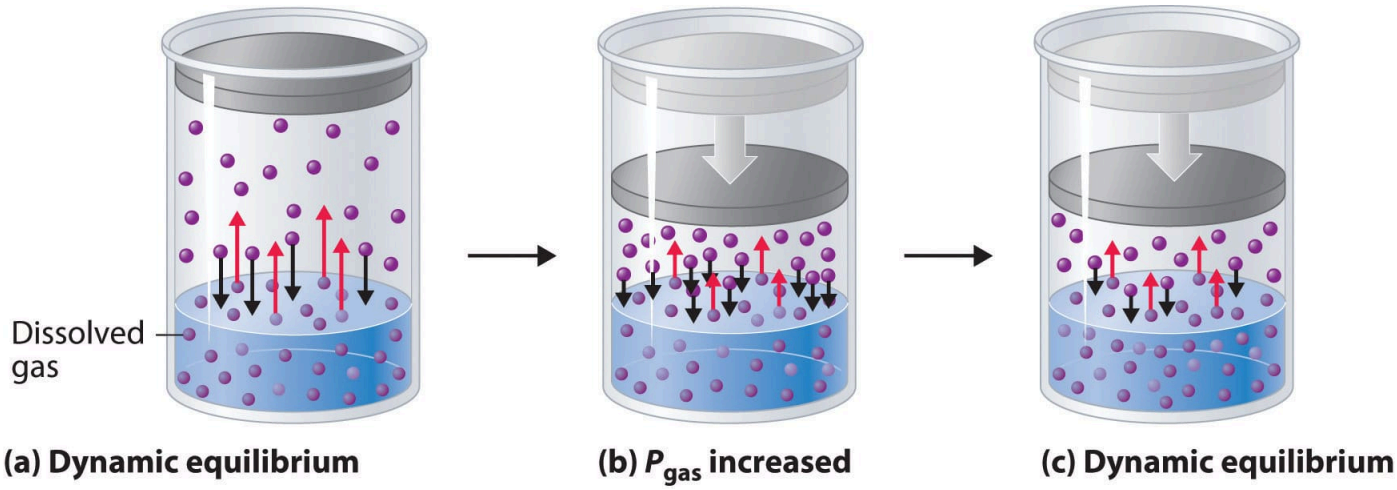


Figure 13.3.4: A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature. (a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established. (CC BY-SA-NC; anonymous)

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

$$C = kP \tag{13.3.2}$$

where

- C is the concentration of dissolved gas at equilibrium,
- P is the partial pressure of the gas, and
- k is the Henry's law constant, which must be determined experimentally for each combination of gas, solvent, and temperature.

Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore mol/(L·atm) = M/atm. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 13.3.1.

As the data in Table 13.3.1 demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the Group 18 elements, the Henry's law constants increase smoothly from He to Ne to Ar.

Table 13.3.1: Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
He	3.9
Ne	4.7
Ar	15
H_2	8.1
N_2	7.1
O_2	14

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
CO_2	392

Oxygen is Especially Soluble

Nitrogen and oxygen are the two most prominent gases in the Earth's atmosphere and they share many similar physical properties. However, as Table $13.3.1$ shows, O_2 is twice as soluble in water as N_2. Many factors contribute to solubility including the nature of the intermolecular forces at play. For a details discussion, see "The O_2/N_2 Ratio Gas Solubility Mystery" by Rubin Battino and Paul G. Seybold (J. Chem. Eng. Data 2011, 56, 5036–5044),

Gases that react chemically with water, such as HCl and the other hydrogen halides, H_2S, and NH_3, do **not** obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give $H^+(aq)$ and $Cl^-(aq)$, not dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule.

> Gases that *react* with water do not obey Henry's law.

Henry's law has important applications. For example, bubbles of CO_2 form as soon as a carbonated beverage is opened because the drink was bottled under CO_2 at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO_2 above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of N_2 to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for O_2 in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O_2 concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O_2 reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O_2 and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O_2 molecules. Although the concentration of dissolved O_2 in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved O_2 concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for O_2 result in dissolved oxygen concentrations comparable to those in normal blood.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

A Video Discussing Henry's Law. Video Link: Henry's Law (The Solubility of Gases in Solvents), YouTube(opens in new window) [youtu.be]

Example $13.3.1$

The Henry's law constant for O_2 in water at 25°C is $1.27 \times 10^{-3} M/atm$, and the mole fraction of O_2 in the atmosphere is 0.21. Calculate the solubility of O_2 in water at 25°C at an atmospheric pressure of 1.00 atm.

Given: Henry's law constant, mole fraction of O_2, and pressure

Asked for: solubility

Strategy:

A. Use Dalton's law of partial pressures to calculate the partial pressure of oxygen. (For more information about Dalton's law of partial pressures)
B. Use Henry's law to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton's law, the partial pressure of O_2 is proportional to the mole fraction of O_2:

$$\begin{aligned} P_A &= \chi_A P_t \\ &= (0.21)(1.00\ atm) \\ &= 0.21\ atm \end{aligned}$$

B From Henry's law, the concentration of dissolved oxygen under these conditions is

$$\begin{aligned} [CO_2] &= kP_{O_2} \\ &= (1.27 \times 10^{-3}\ M/\cancel{atm})(0.21\ \cancel{atm}) \\ &= 2.7 \times 10^{-4}\ M \end{aligned}$$

Exercise 13.3.1

To understand why soft drinks "fizz" and then go "flat" after being opened, calculate the concentration of dissolved CO_2 in a soft drink:

a. bottled under a pressure of 5.0 atm of CO_2
b. in equilibrium with the normal partial pressure of CO_2 in the atmosphere (approximately $3 \times 10^{-4}\ atm$). The Henry's law constant for CO_2 in water at 25°C is $3.4 \times 10^{-2}\ M/atm$.

Answer a available at the end of this section.

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using fractional crystallization, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. Henry's law describes the relationship between the pressure and the solubility of a gas.

Answers

Exercise 13.3.1

$0.17M$

$1 \times 10^{-5}M$

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13.4: Ways of Expressing Concentration

Learning Objectives

- To describe the concentration of a solution in the way that is most appropriate for a particular problem or application.
- To be familiar with the different units used to express the concentrations of a solution.

There are several different ways to quantitatively describe the concentration of a solution. For example, molarity is a useful way to describe solution concentrations for reactions that are carried out in solution. Mole fractions are used not only to describe gas concentrations but also to determine the vapor pressures of mixtures of similar liquids. Example 13.4.1 reviews the methods for calculating the molarity and mole fraction of a solution when the masses of its components are known.

Example 13.4.1: Molarity and Mole Fraction

Commercial vinegar is essentially a solution of acetic acid in water. A bottle of vinegar has 3.78 g of acetic acid per 100.0 g of solution. Assume that the density of the solution is 1.00 g/mL.

a. What is its molarity?
b. What is its mole fraction?

Given: mass of substance and mass and density of solution

Asked for: molarity and mole fraction

Strategy:

A. Calculate the number of moles of acetic acid in the sample. Then calculate the number of liters of solution from its mass and density. Use these results to determine the molarity of the solution.
B. Determine the mass of the water in the sample and calculate the number of moles of water. Then determine the mole fraction of acetic acid by dividing the number of moles of acetic acid by the total number of moles of substances in the sample.

Solution:

A: The molarity is the number of moles of acetic acid per liter of solution. We can calculate the number of moles of acetic acid as its mass divided by its molar mass.

$$\text{moles } CH_3CO_2H = \frac{3.78 \cancel{g}\ CH_3CO_2H}{60.05\ \cancel{g}/\text{mol}}$$

$$= 0.0629 \text{ mol}$$

The volume of the solution equals its mass divided by its density.

$$\text{volume} = \frac{\text{mass}}{\text{density}}$$

$$= \frac{100.0\ \cancel{g}\ \text{solution}}{1.00\ \cancel{g}/m\,\text{L}} = 100\ mL$$

Then calculate the molarity directly.

$$\text{molarity of } CH_3CO_2H = \frac{\text{moles } CH_3CO_2H}{\text{liter solution}}$$
$$= \frac{0.0629\ mol\ CH_3CO_2H}{(100\ \cancel{mL})(1\ L/1000\ \cancel{mL})} = 0.629\ M\ CH_3CO_2H$$

This result makes intuitive sense. If 100.0 g of aqueous solution (equal to 100 mL) contains 3.78 g of acetic acid, then 1 L of solution will contain 37.8 g of acetic acid, which is a little more than $\frac{1}{2}$ mole. Keep in mind, though, that the mass and volume of a solution are related by its density; concentrated aqueous solutions often have densities greater than 1.00 g/mL.

B: To calculate the mole fraction of acetic acid in the solution, we need to know the number of moles of both acetic acid and water. The number of moles of acetic acid is 0.0629 mol, as calculated in part (a). We know that 100.0 g of vinegar contains 3.78 g of acetic acid; hence the solution also contains (100.0 g – 3.78 g) = 96.2 g of water. We have

$$moles\ H_2O = \frac{96.2\ \cancel{g}\ H_2O}{18.02\ \cancel{g}/mol} = 5.34\ mol\ H_2O$$

The mole fraction χ of acetic acid is the ratio of the number of moles of acetic acid to the total number of moles of substances present:

$$\chi_{CH_3CO_2H} = \frac{moles\ CH_3CO_2H}{moles\ CH_3CO_2H + moles\ H_2O}$$
$$= \frac{0.0629\ mol}{0.0629\ mol + 5.34\ mol}$$
$$= 0.0116 = 1.16 \times 10^{-2}$$

This answer makes sense, too. There are approximately 100 times as many moles of water as moles of acetic acid, so the ratio should be approximately 0.01.

Exercise 13.4.1: Molarity and Mole Fraction

A solution of HCl gas dissolved in water (sold commercially as “muriatic acid,” a solution used to clean masonry surfaces) has 20.22 g of HCl per 100.0 g of solution, and its density is 1.10 g/mL.

a. What is its molarity?
b. What is its mole fraction?

Answer a available at the end of this section.

The concentration of a solution can also be described by its molality (m), the number of moles of solute per kilogram of solvent:

$$\text{molality (m)} = \frac{\text{moles solute}}{\text{kilogram solvent}} \tag{13.4.1}$$

Molality, therefore, has the same numerator as molarity (the number of moles of solute) but a different denominator (kilogram of solvent rather than liter of solution). For dilute aqueous solutions, the molality and molarity are nearly the same because dilute solutions are mostly solvent. Thus because the density of water under standard conditions is very close to 1.0 g/mL, the volume of 1.0 kg of H_2O under these conditions is very close to 1.0 L, and a 0.50 M solution of KBr in water, for example, has approximately the same concentration as a 0.50 m solution.

Another common way of describing concentration is as the ratio of the mass of the solute to the total mass of the solution. The result can be expressed as mass percentage, parts per million (ppm), or parts per billion (ppb):

$$\text{mass percentage} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \tag{13.4.2}$$

$$\text{parts per million (ppm)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \tag{13.4.3}$$

$$\text{parts per billion (ppb)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \tag{13.4.4}$$

In the health sciences, the concentration of a solution is often expressed as parts per thousand (ppt), indicated as a proportion. For example, adrenalin, the hormone produced in high-stress situations, is available in a 1:1000 solution, or one gram of adrenalin per 1000 g of solution.

The labels on bottles of commercial reagents often describe the contents in terms of mass percentage. Sulfuric acid, for example, is sold as a 95% aqueous solution, or 95 g of H_2SO_4 per 100 g of solution. Parts per million and parts per billion are used to describe concentrations of highly dilute solutions. These measurements correspond to milligrams and micrograms of solute per kilogram of solution, respectively. For dilute aqueous solutions, this is equal to milligrams and micrograms of solute per liter of solution (assuming a density of 1.0 g/mL).

Example 13.4.2: Molarity and Mass

Several years ago, millions of bottles of mineral water were contaminated with benzene at ppm levels. This incident received a great deal of attention because the lethal concentration of benzene in rats is 3.8 ppm. A 250 mL sample of mineral water has 12.7 ppm of benzene. Because the contaminated mineral water is a very dilute aqueous solution, we can assume that its density is approximately 1.00 g/mL.

a. What is the molarity of the solution?
b. What is the mass of benzene in the sample?

Given: volume of sample, solute concentration, and density of solution

Asked for: molarity of solute and mass of solute in 250 mL

Strategy:

A. Use the concentration of the solute in parts per million to calculate the molarity.
B. Use the concentration of the solute in parts per million to calculate the mass of the solute in the specified volume of solution.

Solution:

a. A To calculate the molarity of benzene, we need to determine the number of moles of benzene in 1 L of solution. We know that the solution contains 12.7 ppm of benzene. Because 12.7 ppm is equivalent to 12.7 mg/1000 g of solution and the density of the solution is 1.00 g/mL, the solution contains 12.7 mg of benzene per liter (1000 mL). The molarity is therefore

$$\begin{aligned}\text{molarity} &= \frac{\text{moles}}{\text{liter solution}} \\ &= \frac{(12.7\ \cancel{mg})\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{78.114\ \cancel{g}}\right)}{1.00\ L} \\ &= 1.63 \times 10^{-4} M\end{aligned}$$

b. B We are given that there are 12.7 mg of benzene per 1000 g of solution, which is equal to 12.7 mg/L of solution. Hence the mass of benzene in 250 mL (250 g) of solution is

$$\begin{aligned}\text{mass of benzene} &= \frac{(12.7\ mg\ \text{benzene})(250\ \cancel{mL})}{1000\ \cancel{mL}} \\ &= 3.18\ mg \\ &= 3.18 \times 10^{-3}\ g\ \text{benzene}\end{aligned}$$

Exercise 13.4.2: Molarity of Lead Solution

The maximum allowable concentration of lead in drinking water is 9.0 ppb.

a. What is the molarity of Pb^{2+} in a 9.0 ppb aqueous solution?
b. Use your calculated concentration to determine how many grams of Pb^{2+} are in an 8 oz glass of water.

Answer a available at the end of this section.

How do chemists decide which units of concentration to use for a particular application? Although molarity is commonly used to express concentrations for reactions in solution or for titrations, it does have one drawback—molarity is the number of moles of solute divided by the volume of the solution, and the volume of a solution depends on its density, which is a function of temperature. Because volumetric glassware is calibrated at a particular temperature, typically 20°C, the molarity may differ from the original value by several percent if a solution is prepared or used at a significantly different temperature, such as 40°C or 0°C. For many applications this may not be a problem, but for precise work these errors can become important. In contrast, mole fraction, molality, and mass percentage depend on only the masses of the solute and solvent, which are independent of temperature.

Mole fraction is not very useful for experiments that involve quantitative reactions, but it is convenient for calculating the partial pressure of gases in mixtures, as discussed previously. Mole fractions are also useful for calculating the vapor pressures of certain types of solutions. Molality is particularly useful for determining how properties such as the freezing or boiling point of a solution vary with solute concentration. Because mass percentage and parts per million or billion are simply different ways of expressing the ratio of the mass of a solute to the mass of the solution, they enable us to express the concentration of a substance even when the molecular mass of the substance is unknown. Units of ppb or ppm are also used to express very low concentrations, such as those of residual impurities in foods or of pollutants in environmental studies.

Table 13.4.1 summarizes the different units of concentration and typical applications for each. When the molar mass of the solute and the density of the solution are known, it becomes relatively easy with practice to convert among the units of concentration we have discussed, as illustrated in Example 13.4.3.

*Table 13.4.1: Different Units for Expressing the Concentrations of Solutions**

Unit	Definition	Application
molarity (M)	moles of solute/liter of solution (mol/L)	Used for quantitative reactions in solution and titrations; mass and molecular mass of solute and volume of solution are known.
mole fraction (χ)	moles of solute/total moles present (mol/mol)	Used for partial pressures of gases and vapor pressures of some solutions; mass and molecular mass of each component are known.
molality (m)	moles of solute/kg of solvent (mol/kg)	Used in determining how colligative properties vary with solute concentration; masses and molecular mass of solute are known.
mass percentage (%)	[mass of solute (g)/mass of solution (g)] × 100	Useful when masses are known but molecular masses are unknown.
parts per thousand (ppt)	[mass of solute/mass of solution] × 10^3 (g solute/kg solution)	Used in the health sciences, ratio solutions are typically expressed as a proportion, such as 1:1000.
parts per million (ppm)	[mass of solute/mass of solution] × 10^6 (mg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
parts per billion (ppb)	[mass of solute/mass of solution] × 10^9 (µg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
***The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.**		

Example 13.4.3: Vodka

Vodka is essentially a solution of ethanol in water. Typical vodka is sold as "80 proof," which means that it contains 40.0% ethanol by volume. The density of pure ethanol is 0.789 g/mL at 20°C. If we assume that the volume of the solution is the sum of the volumes of the components (which is not strictly correct), calculate the following for the ethanol in 80-proof vodka.

a. the mass percentage
b. the mole fraction
c. the molarity
d. the molality

Given: volume percent and density

Asked for: mass percentage, mole fraction, molarity, and molality

Strategy:

A. Use the density of the solute to calculate the mass of the solute in 100.0 mL of solution. Calculate the mass of water in 100.0 mL of solution.
B. Determine the mass percentage of solute by dividing the mass of ethanol by the mass of the solution and multiplying by 100.
C. Convert grams of solute and solvent to moles of solute and solvent. Calculate the mole fraction of solute by dividing the moles of solute by the total number of moles of substances present in solution.
D. Calculate the molarity of the solution: moles of solute per liter of solution. Determine the molality of the solution by dividing the number of moles of solute by the kilograms of solvent.

Solution:

The key to this problem is to use the density of pure ethanol to determine the mass of ethanol (CH_3CH_2OH), abbreviated as EtOH, in a given volume of solution. We can then calculate the number of moles of ethanol and the concentration of ethanol in any of the required units. A Because we are given a percentage by volume, we assume that we have 100.0 mL of solution. The volume of ethanol will thus be 40.0% of 100.0 mL, or 40.0 mL of ethanol, and the volume of water will be 60.0% of 100.0 mL, or 60.0 mL of water. The mass of ethanol is obtained from its density:

$$mass\ of\ EtOH = (40.0\ \cancel{mL}) \left(\frac{0.789\ g}{\cancel{mL}} \right) = 31.6\ g\ EtOH$$

If we assume the density of water is 1.00 g/mL, the mass of water is 60.0 g. We now have all the information we need to calculate the concentration of ethanol in the solution.

B The mass percentage of ethanol is the ratio of the mass of ethanol to the total mass of the solution, expressed as a percentage:

$$\begin{aligned} \%EtOH &= \left(\frac{mass\ of\ EtOH}{mass\ of\ solution} \right) (100) \\ &= \left(\frac{31.6\ \cancel{g}\ EtOH}{31.6\ \cancel{g}\ EtOH + 60.0\ \cancel{g}\ H_2O} \right) (100) \\ &= 34.5\% \end{aligned}$$

C The mole fraction of ethanol is the ratio of the number of moles of ethanol to the total number of moles of substances in the solution. Because 40.0 mL of ethanol has a mass of 31.6 g, we can use the molar mass of ethanol (46.07 g/mol) to determine the number of moles of ethanol in 40.0 mL:

$$\begin{aligned} moles\ \mathrm{CH_3CH_2OH} &= (31.6\ \cancel{g\ \mathrm{CH_3CH_2OH}}) \left(\frac{1\ mol}{46.07\ \cancel{g\ \mathrm{CH_3CH_2OH}}} \right) \\ &= 0.686\ mol\ \mathrm{CH_3CH_2OH} \end{aligned}$$

Similarly, the number of moles of water is

$$moles\ H_2O = (60.0\ \cancel{g\ H_2O}) \left(\frac{1\ mol\ H_2O}{18.02\ \cancel{g\ H_2O}} \right) = 3.33\ mol\ H_2O$$

The mole fraction of ethanol is thus

$$\chi_{CH_3CH_2OH} = \frac{0.686\ \cancel{mol}}{0.686\ \cancel{mol} + 3.33\ \cancel{mol}} = 0.171$$

D The molarity of the solution is the number of moles of ethanol per liter of solution. We already know the number of moles of ethanol per 100.0 mL of solution, so the molarity is

$$M_{CH_3CH_2OH} = \left(\frac{0.686\ mol}{100\ \cancel{mL}} \right) \left(\frac{1000\ \cancel{mL}}{L} \right) = 6.86\ M$$

The molality of the solution is the number of moles of ethanol per kilogram of solvent. Because we know the number of moles of ethanol in 60.0 g of water, the calculation is again straightforward:

$$m_{CH_3CH_2OH} = \left(\frac{0.686\ mol\ EtOH}{60.0\ \cancel{g}\ H_2O} \right) \left(\frac{1000\ \cancel{g}}{kg} \right) = \frac{11.4\ mol\ EtOH}{kg\ H_2O} = 11.4\ m$$

Exercise 13.4.3: Toluene/Benzene Solution

A solution is prepared by mixing 100.0 mL of toluene with 300.0 mL of benzene. The densities of toluene and benzene are 0.867 g/mL and 0.874 g/mL, respectively. Assume that the volume of the solution is the sum of the volumes of the components. Calculate the following for toluene.

a. mass percentage
b. mole fraction
c. molarity
d. molality

Answer a available at the end of this section.

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Summary

Different units are used to express the concentrations of a solution depending on the application. The concentration of a solution is the quantity of solute in a given quantity of solution. It can be expressed in several ways: molarity (moles of solute per liter of solution); mole fraction, the ratio of the number of moles of solute to the total number of moles of substances present; mass percentage, the ratio of the mass of the solute to the mass of the solution times 100; parts per thousand (ppt), grams of solute per kilogram of solution; parts per million (ppm), milligrams of solute per kilogram of solution; parts per billion (ppb), micrograms of solute per kilogram of solution; and molality (m), the number of moles of solute per kilogram of solvent.

Answers

Exercise 13.4.1**: Molarity and Mole Fraction**

6.10 M HCl

$\chi_{HCl} = 0.111$

Exercise 13.4.2**: Molarity of Lead Solution**

4.3×10^{-8} M

2×10^{-6} g

Exercise 13.4.3**: Toluene/Benzene Solution**

mass percentage toluene = 24.8%

$\chi_{toluene} = 0.219$

2.35 M toluene

3.59 m toluene

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13.5: Colligative Properties

Learning Objectives

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Many of the physical properties of solutions differ significantly from those of the pure substances discussed in earlier chapters, and these differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) severely limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol ("antifreeze") to the water in an automobile radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode.

Changes in the freezing point and boiling point of a solution depend primarily on the number of solute particles present rather than the kind of particles. Such properties of solutions are called colligative properties (from the Latin colligatus, meaning "bound together" as in a quantity). As we will see, the vapor pressure and osmotic pressure of solutions are also colligative properties.

Counting concentrations

When we determine the number of particles in a solution, it is important to remember that not all solutions with the same molarity contain the same concentration of solute particles. Consider, for example, 0.01 M aqueous solutions of sucrose, NaCl, and $\mathrm{CaCl_2}$. Because sucrose dissolves to give a solution of neutral molecules, the concentration of solute particles in a 0.01 M sucrose solution is 0.01 M. In contrast, both NaCl and $\mathrm{CaCl_2}$ are ionic compounds that dissociate in water to yield solvated ions. As a result, a 0.01 M aqueous solution of NaCl contains 0.01 M $\mathrm{Na^+}$ ions and 0.01 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.02 M. Similarly, the $\mathrm{CaCl_2}$ solution contains 0.01 M $\mathrm{Ca^{2+}}$ ions and 0.02 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.03 M. These values are correct for dilute solutions, where the dissociation of the compounds to form separately solvated ions is complete.

At **higher concentrations** (typically >1 M), especially with salts of small, highly charged ions (such as $\mathrm{Mg^{2+}}$ or $\mathrm{Al^{3+}}$), or in solutions with less polar solvents, dissociation to give separate ions is often incomplete. The sum of the concentrations of the dissolved solute particles dictates the physical properties of a solution. In the following discussion, we must therefore keep the chemical nature of the solute firmly in mind.

Vapor Pressure of Solutions and Raoult's Law

Adding a nonvolatile solute, one whose vapor pressure is too low to measure readily, to a volatile solvent decreases the vapor pressure of the solvent. We can understand this phenomenon qualitatively by examining Figure $13.5.1$, which is a schematic diagram of the surface of a solution of glucose in water. In an aqueous solution of glucose, a portion of the surface area is occupied by nonvolatile glucose molecules rather than by volatile water molecules. As a result, fewer water molecules can enter the vapor phase per unit time, even though the surface water molecules have the same kinetic energy distribution as they would in pure water. At the same time, the rate at which water molecules in the vapor phase collide with the surface and reenter the solution is unaffected. The net effect is to shift the dynamic equilibrium between water in the vapor and the liquid phases, decreasing the vapor pressure of the solution compared with the vapor pressure of the pure solvent.

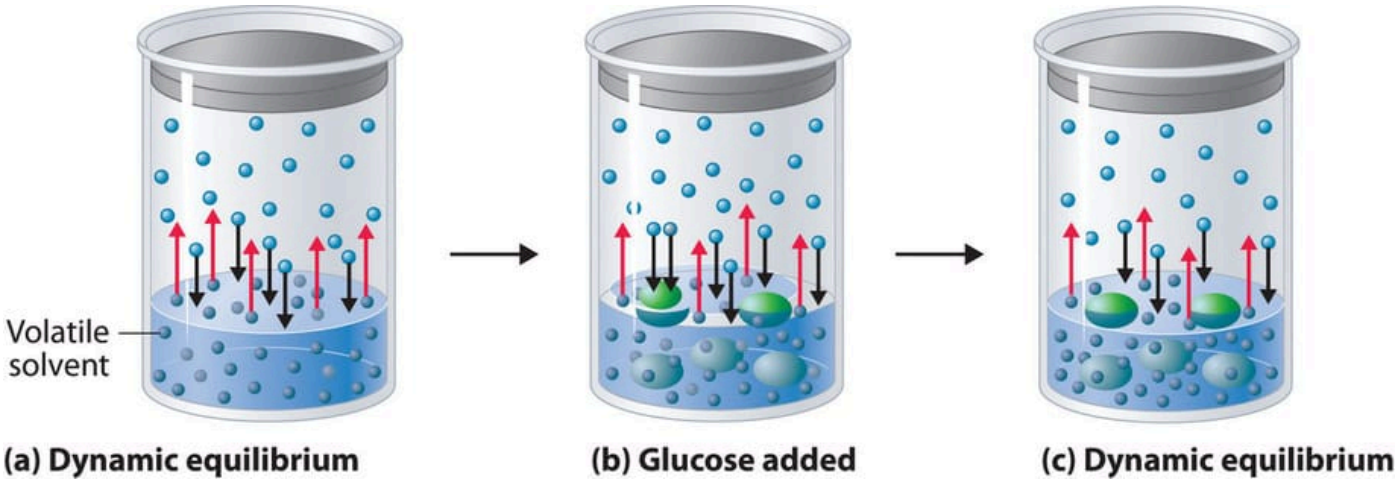


Figure 13.5.1: A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water. (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile solute such as glucose is added, some fraction of the surface area is occupied by solvated solute molecules. As a result, the rate at which water molecules evaporate is decreased, although initially their rate of condensation is unchanged. (c) When the glucose solution reaches equilibrium, the concentration of water molecules in the vapor phase, and hence the vapor pressure, is less than that of pure water.

Figure 13.5.2 shows two beakers, one containing pure water and one containing an aqueous glucose solution, in a sealed chamber. We can view the system as having two competing equilibria: water vapor will condense in both beakers at the same rate, but water molecules will evaporate more slowly from the glucose solution because fewer water molecules are at the surface. Eventually all of the water will evaporate from the beaker containing the liquid with the higher vapor pressure (pure water) and condense in the beaker containing the liquid with the lower vapor pressure (the glucose solution). If the system consisted of only a beaker of water inside a sealed container, equilibrium between the liquid and vapor would be achieved rather rapidly, and the amount of liquid water in the beaker would remain constant.

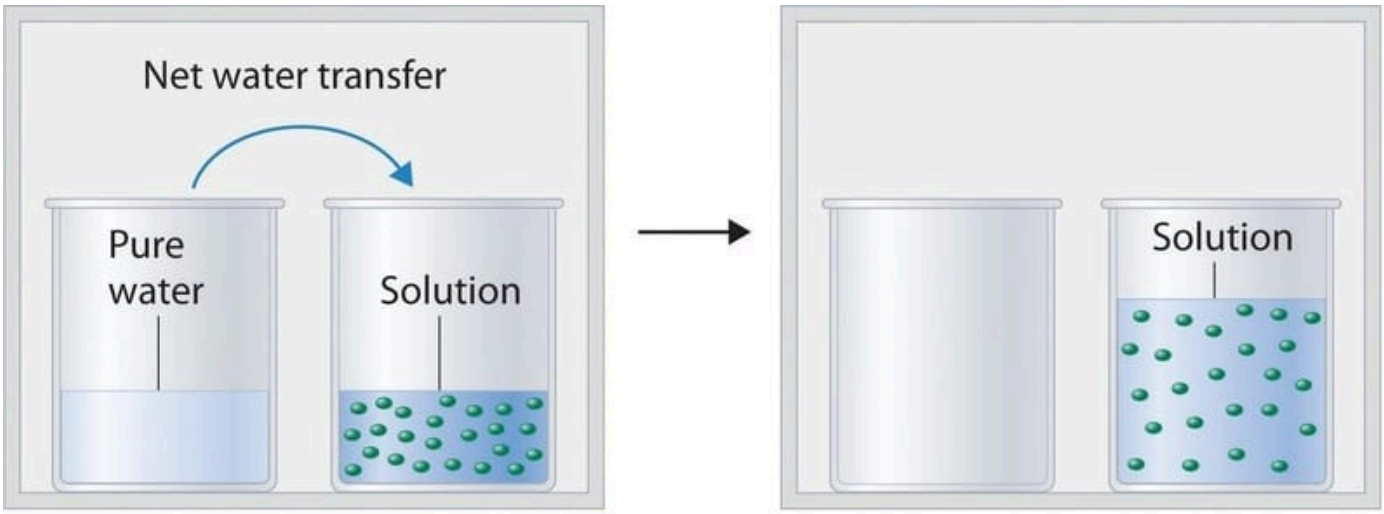


Figure 13.5.2: Transfer of Water to a Beaker Containing a Glucose Solution. (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water from the beaker containing pure water to the beaker containing the glucose solution. (bottom) Eventually, all of the water is transferred to the beaker that has the glucose solution.

If the particles of a solute are essentially the same size as those of the solvent and both solute and solvent have roughly equal probabilities of being at the surface of the solution, then the effect of a solute on the vapor pressure of the solvent is proportional to the number of sites occupied by solute particles at the surface of the solution. Doubling the concentration of a given solute causes twice as many surface sites to be occupied by solute molecules, resulting in twice the decrease in vapor pressure. The relationship between solution composition and vapor pressure is therefore

$$P_A = \chi_A P_A^0 \tag{13.5.1}$$

where P_A is the vapor pressure of component A of the solution (in this case the solvent), χ_A is the mole fraction of A in solution, and P_A^0 is the vapor pressure of pure A. Equation 13.5.1 is known as **Raoult's law**, after the French chemist who developed it. If the solution contains only a single nonvolatile solute (B), then $\chi_A + \chi_B = 1$, and we can substitute $\chi_A = 1 - \chi_B$ to obtain

$$P_A = (1 - \chi_B)P_A^0 \tag{13.5.2}$$

$$= P_A^0 - \chi_B P_A^0 \tag{13.5.3}$$

Rearranging and defining $\Delta P_A = P_A^0 - P_A$, we obtain a relationship between the decrease in vapor pressure and the mole fraction of nonvolatile solute:

$$P_A^0 - P_A = \Delta P_A \tag{13.5.4}$$

$$= \chi_B P_A^0 \tag{13.5.5}$$

We can solve vapor pressure problems in either of two ways: by using Equation 13.5.1 to calculate the actual vapor pressure above a solution of a nonvolatile solute, or by using Equation 13.5.5 to calculate the decrease in vapor pressure caused by a specified amount of a nonvolatile solute.

Example 13.5.1: Anti-Freeze

Ethylene glycol ($HOCH_2CH_2OH$), the major ingredient in commercial automotive antifreeze, increases the boiling point of radiator fluid by lowering its vapor pressure. At 100°C, the vapor pressure of pure water is 760 mmHg. Calculate the vapor pressure of an aqueous solution containing 30.2% ethylene glycol by mass, a concentration commonly used in climates that do not get extremely cold in winter.

Given: identity of solute, percentage by mass, and vapor pressure of pure solvent

Asked for: vapor pressure of solution

Strategy:

A. Calculate the number of moles of ethylene glycol in an arbitrary quantity of water, and then calculate the mole fraction of water.
B. Use Raoult's law to calculate the vapor pressure of the solution.

Solution:

A A 30.2% solution of ethylene glycol contains 302 g of ethylene glycol per kilogram of solution; the remainder (698 g) is water. To use Raoult's law to calculate the vapor pressure of the solution, we must know the mole fraction of water. Thus we must first calculate the number of moles of both ethylene glycol (EG) and water present:

$$moles\ EG = (302\ \cancel{g})\left(\frac{1\ mol}{62.07\ \cancel{g}}\right) = 4.87\ mol\ EG$$

$$moles\ H_2O = (698\ \cancel{g})\left(\frac{1\ mol}{18.02\ \cancel{g}}\right) = 38.7\ mol\ H_2O$$

The mole fraction of water is thus

$$\chi_{H_2O} = \frac{38.7\ \cancel{mol}\ H_2O}{38.7\ \cancel{mol}\ H_2O + 4.87\ \cancel{mol}\ EG} = 0.888$$

B From Raoult's law (Equation 13.5.1), the vapor pressure of the solution is

$$P_{H_2O} = (\chi_{H2_O})(P^0_{H_2O})$$

$$= (0.888)(760\ mmHg) = 675\ mmHg$$

Alternatively, we could solve this problem by calculating the mole fraction of ethylene glycol and then using Equation 13.5.5 to calculate the resulting decrease in vapor pressure:

$$\chi_{EG} = \frac{4.87\ mol\ EG}{4.87\ mol\ EG + 38.7\ mol\ H_2O} = 0.112$$

$$\Delta P_{H2_O} = (\chi_{EG})(P^0_{H_2O}) = (0.112)(760\ mmHg) = 85.1\ mmHg$$

$$P_{H_2O} = P^0_{H_2O} - \Delta P_{H_2O} = 760\ mmHg - 85.1\ mmHg = 675\ mmHg$$

The same result is obtained using either method.

Exercise 13.5.1

Seawater is an approximately 3.0% aqueous solution of NaCl by mass with about 0.5% of other salts by mass. Calculate the decrease in the vapor pressure of water at 25°C caused by this concentration of NaCl, remembering that 1 mol of NaCl produces 2 mol of solute particles. The vapor pressure of pure water at 25°C is 23.8 mmHg.

Answer available at the end of this section.

Even when a solute is volatile, meaning that it has a measurable vapor pressure, we can still use Raoult's law. In this case, we calculate the vapor pressure of each component separately. The total vapor pressure of the solution (P_{tot}) is the sum of the vapor pressures of the components:

$$P_{tot} = P_A + P_B = \chi_A P^0_A + \chi_B P^0_B \tag{13.5.6}$$

Because $\chi_B = 1 - \chi_A$ for a two-component system,

$$P_{tot} = \chi_A P^0_A + (1 - \chi_A) P^0_B \tag{13.5.7}$$

Thus we need to specify the mole fraction of only one of the components in a two-component system. Consider, for example, the vapor pressure of solutions of benzene and toluene of various compositions. At 20°C, the vapor pressures of pure benzene and toluene are 74.7 and 22.3 mmHg, respectively. The vapor pressure of benzene in a benzene–toluene solution is

$$P_{C_6H_6} = \chi_{C_6H_6} P^0_{C_6H_6} \tag{13.5.8}$$

and the vapor pressure of toluene in the solution is

$$PC_6H_5CH_3 = \chi_{C_6H_5CH_3} P^0_{C_6H_5CH3} \tag{13.5.9}$$

Equations 13.5.8 and 13.5.9 are both in the form of the equation for a straight line: $y = mx + b$, where $b = 0$. Plots of the vapor pressures of both components versus the mole fractions are therefore straight lines that pass through the origin, as shown in Figure 13.5.3. Furthermore, a plot of the total vapor pressure of the solution versus the mole fraction is a straight line that represents the sum of the vapor pressures of the pure components. Thus the vapor pressure of the solution is always greater than the vapor pressure of either component.

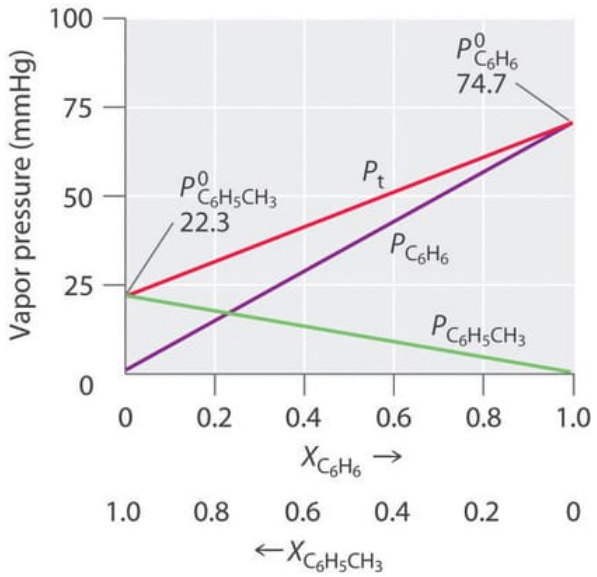


Figure 13.5.3: Vapor Pressures of Benzene–Toluene Solutions. Plots of the vapor pressures of benzene (C_6H_6) and toluene ($C_6H_5CH_3$) versus the mole fractions at 20°C are straight lines. For a solution like this, which approximates an ideal solution, the total vapor pressure of the solution (P_{tot}) is the sum of the vapor pressures of the components.

Graph of vapp pressure in mmHg against benzene and toulen mole fractions. Benzene mole fractions increase from left to right while toluene mole fractions decrease from left to right on the x axis.

A solution of two volatile components that behaves like the solution in Figure 13.5.3, which is defined as a solution that obeys Raoult's law. Like an ideal gas, an ideal solution is a hypothetical system whose properties can be described in terms of a simple model. Mixtures of benzene and toluene approximate an ideal solution because the intermolecular forces in the two pure liquids are almost identical in both kind and magnitude. Consequently, the change in enthalpy on solution formation is essentially zero ($\Delta H_{soln} \approx 0$), which is one of the defining characteristics of an ideal solution.

> Ideal solutions and ideal gases are both simple models that ignore intermolecular interactions.

Most real solutions, however, do not obey Raoult's law precisely, just as most real gases do not obey the ideal gas law exactly. Real solutions generally deviate from Raoult's law because the intermolecular interactions between the two components A and B differ. We can distinguish between two general kinds of behavior, depending on whether the intermolecular interactions between molecules A and B are stronger or weaker than the A–A and B–B interactions in the pure components. If the A–B interactions are stronger than the A–A and B–B interactions, each component of the solution exhibits a lower vapor pressure than expected for an ideal solution, as does the solution as a whole. The favorable A–B interactions effectively stabilize the solution compared with the vapor. This kind of behavior is called a negative deviation from Raoult's law. Systems stabilized by hydrogen bonding between two molecules, such as acetone and ethanol, exhibit **negative deviations** from Raoult's law. Conversely, if the A–B interactions are weaker than the A–A and B–B interactions yet the entropy increase is enough to allow the solution to form, both A and B have an increased tendency to escape from the solution into the vapor phase. The result is a higher vapor pressure than expected for an ideal solution, producing a positive deviation from Raoult's law. In a solution of CCl_4 and methanol, for example, the nonpolar CCl_4 molecules interrupt the extensive hydrogen bonding network in methanol, and the lighter methanol molecules have weaker London dispersion forces than the heavier CCl_4 molecules. Consequently, solutions of CCl_4 and methanol exhibit **positive deviations** from Raoult's law.

Example 13.5.2

For each system, compare the intermolecular interactions in the pure liquids and in the solution to decide whether the vapor pressure will be greater than that predicted by Raoult's law (positive deviation), approximately equal to that predicted by Raoult's law (an ideal solution), or less than the pressure predicted by Raoult's law (negative deviation).

a. cyclohexane and ethanol
b. methanol and acetone

c. n-hexane and isooctane (2,2,4-trimethylpentane)

Given: identity of pure liquids

Asked for: predicted deviation from Raoult's law (Equation 13.5.1)

Strategy:

Identify whether each liquid is polar or nonpolar, and then predict the type of intermolecular interactions that occur in solution.

Solution:

a. Liquid ethanol contains an extensive hydrogen bonding network, and cyclohexane is nonpolar. Because the cyclohexane molecules cannot interact favorably with the polar ethanol molecules, they will disrupt the hydrogen bonding. Hence the A–B interactions will be weaker than the A–A and B–B interactions, leading to a higher vapor pressure than predicted by Raoult's law (a positive deviation).
b. Methanol contains an extensive hydrogen bonding network, but in this case the polar acetone molecules create A–B interactions that are stronger than the A–A or B–B interactions, leading to a negative enthalpy of solution and a lower vapor pressure than predicted by Raoult's law (a negative deviation).
c. Hexane and isooctane are both nonpolar molecules (isooctane actually has a very small dipole moment, but it is so small that it can be ignored). Hence the predominant intermolecular forces in both liquids are London dispersion forces. We expect the A–B interactions to be comparable in strength to the A–A and B–B interactions, leading to a vapor pressure in good agreement with that predicted by Raoult's law (an ideal solution).

Exercise 13.5.2

For each system, compare the intermolecular interactions in the pure liquids with those in the solution to decide whether the vapor pressure will be greater than that predicted by Raoult's law (positive deviation), approximately equal to that predicted by Raoult's law (an ideal solution), or less than the pressure predicted by Raoult's law (negative deviation):

a. benzene and n-hexane
b. ethylene glycol and CCl_4
c. acetic acid and n-propanol

Answer a available at the end of this section.

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A Video Discussing Roult's Law. Video Link: Introduction to the Vapor Pressure of a Solution (Raoult's Law), YouTube(opens in new window) [youtu.be]

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A Video Discussing How to find the Vapor Pressure of a Solution. Video Link: Finding the Vapor Pressure of a Solution (Nonionic-Nonvolatile Solute), YouTube(opens in new window) [youtu.be]

Boiling Point Elevation

Recall that the normal boiling point of a substance is the temperature at which the vapor pressure equals 1 atm. If a nonvolatile solute lowers the vapor pressure of a solvent, it must also affect the boiling point. Because the vapor pressure of the solution at a given temperature is less than the vapor pressure of the pure solvent, achieving a vapor pressure of 1 atm for the solution requires a higher temperature than the normal boiling point of the solvent. Thus the boiling point of a solution is always greater than that of the pure solvent. We can see why this must be true by comparing the phase diagram for an aqueous solution with the phase diagram for pure water (Figure 13.5.4). The vapor pressure of the solution is less than that of pure water at all temperatures. Consequently, the liquid–vapor curve for the solution crosses the horizontal line corresponding to P = 1 atm at a higher temperature than does the curve for pure water.

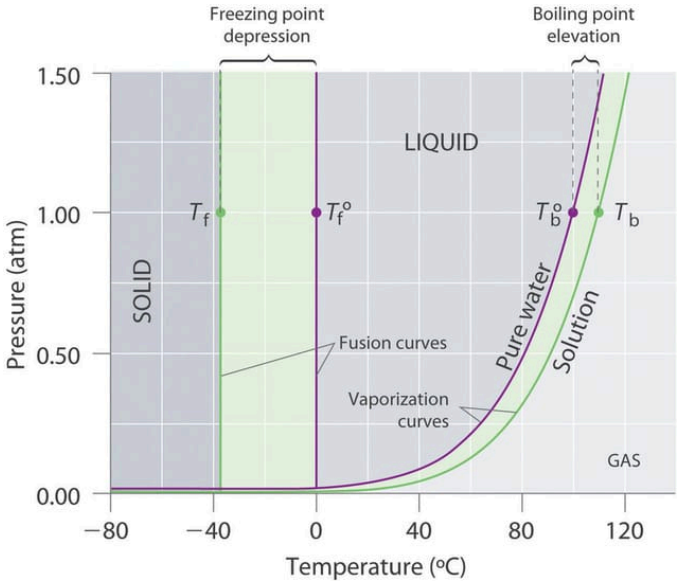


Figure 13.5.4: Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute. The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution.

The boiling point of a solution with a nonvolatile solute is **always** greater than the boiling point of the pure solvent.

The magnitude of the increase in the boiling point is related to the magnitude of the decrease in the vapor pressure. As we have just discussed, the decrease in the vapor pressure is proportional to the concentration of the solute in the solution. Hence the magnitude of the increase in the boiling point must also be proportional to the concentration of the solute (Figure 13.5.5).

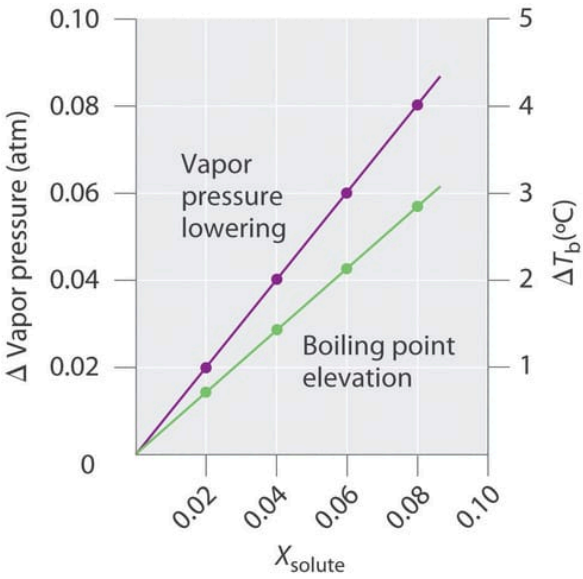


Figure 13.5.5: Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute
Change in vapor pressure in atm in on the left side y axis while change in temperature is on the right side y axis. These are being plotted against mole fraction of solute.

We can define the boiling point elevation (ΔT_b) as the difference between the boiling points of the solution and the pure solvent:

$$\Delta T_b = T_b - T_b^0 \tag{13.5.10}$$

where T_b is the boiling point of the solution and T_b^0 is the boiling point of the pure solvent. We can express the relationship between ΔT_b and concentration as follows

$$\Delta T_b = mK_b \tag{13.5.11}$$

where m is the concentration of the solute expressed in molality, and K_b is the **molal boiling point elevation constant** of the solvent, which has units of °C/m. Table 13.5.1 lists characteristic K_b values for several commonly used solvents. For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

Table 13.5.1: Boiling Point Elevation Constants (K_b) and Freezing Point Depression Constants (K_f) for Some Solvents

Solvent	Boiling Point (°C)	K_b (°C/m)	Freezing Point (°C)	K_f (°C/m)
acetic acid	117.90	3.22	16.64	3.63
benzene	80.09	2.64	5.49	5.07
d-(+)-camphor	207.4	4.91	178.8	37.8
carbon disulfide	46.2	2.42	–112.1	3.74
carbon tetrachloride	76.8	5.26	–22.62	31.4
chloroform	61.17	3.80	–63.41	4.60
nitrobenzene	210.8	5.24	5.70	6.87
water	100.00	0.51	0.00	1.86

The concentration of the solute is typically expressed as molality rather than mole fraction or molarity for two reasons. First, because the density of a solution changes with temperature, the value of molarity also varies with temperature. If the boiling point depends on the solute concentration, then by definition the system is not maintained at a constant temperature. Second, molality and mole fraction are proportional for relatively dilute solutions, but molality has a larger numerical value (a mole fraction can be only between zero and one). Using molality allows us to eliminate nonsignificant zeros.

According to Table 13.5.1, the molal boiling point elevation constant for water is 0.51°C/m. Thus a 1.00 m aqueous solution of a

nonvolatile molecular solute such as glucose or sucrose will have an increase in boiling point of 0.51°C, to give a boiling point of 100.51°C at 1.00 atm. The increase in the boiling point of a 1.00 m aqueous NaCl solution will be approximately twice as large as that of the glucose or sucrose solution because 1 mol of NaCl produces 2 mol of dissolved ions. Hence a 1.00 m NaCl solution will have a boiling point of about 101.02°C.

Example 13.5.3

In Example 13.5.1, we calculated that the vapor pressure of a 30.2% aqueous solution of ethylene glycol at 100°C is 85.1 mmHg less than the vapor pressure of pure water. We stated (without offering proof) that this should result in a higher boiling point for the solution compared with pure water. Now that we have seen why this assertion is correct, calculate the boiling point of the aqueous ethylene glycol solution.

Given: composition of solution

Asked for: boiling point

Strategy:

Calculate the molality of ethylene glycol in the 30.2% solution. Then use Equation 13.5.11 to calculate the increase in boiling point.

Solution:

From Example 13.5.1, we know that a 30.2% solution of ethylene glycol in water contains 302 g of ethylene glycol (4.87 mol) per 698 g of water. The molality of the solution is thus

$$\text{molality of ethylene glycol} = \left(\frac{4.87\ mol}{698\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.98\,m$$

From Equation 13.5.11, the increase in boiling point is therefore

$$\Delta T_b = mK_b = (6.98\,\cancel{m})(0.51°C/\cancel{m}) = 3.6°C$$

The boiling point of the solution is thus predicted to be 104°C. With a solute concentration of almost 7 m, however, the assumption of a dilute solution used to obtain Equation 13.5.11 may not be valid.

Exercise 13.5.3

Assume that a tablespoon (5.00 g) of NaCl is added to 2.00 L of water at 20.0°C, which is then brought to a boil to cook spaghetti. At what temperature will the water boil?

Answer available at the end of this section.

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A Video Discussing Boiling Point Elevation and Freezing Point Depression. Video Link: Boiling Point Elevation and Freezing Point Depression, YouTube(opens in new window) [youtu.be] (opens in new window)

Freezing Point Depression

The phase diagram in Figure $13.5.4$ shows that dissolving a nonvolatile solute in water not only raises the boiling point of the water but also lowers its freezing point. The solid–liquid curve for the solution crosses the line corresponding to $P = 1\ atm$ at a lower temperature than the curve for pure water.

We can understand this result by imagining that we have a sample of water at the normal freezing point temperature, where there is a dynamic equilibrium between solid and liquid. Water molecules are continuously colliding with the ice surface and entering the solid phase at the same rate that water molecules are leaving the surface of the ice and entering the liquid phase. If we dissolve a nonvolatile solute such as glucose in the liquid, the dissolved glucose molecules will reduce the number of collisions per unit time between water molecules and the ice surface because some of the molecules colliding with the ice will be glucose. Glucose, though, has a very different structure than water, and it cannot fit into the ice lattice. Consequently, the presence of glucose molecules in the solution can only decrease the rate at which water molecules in the liquid collide with the ice surface and solidify. Meanwhile, the rate at which the water molecules leave the surface of the ice and enter the liquid phase is unchanged. The net effect is to cause the ice to melt. The only way to reestablish a dynamic equilibrium between solid and liquid water is to lower the temperature of the system, which decreases the rate at which water molecules leave the surface of the ice crystals until it equals the rate at which water molecules in the solution collide with the ice.

By analogy to our treatment of boiling point elevation,the freezing point depression (ΔT_f) is defined as the difference between the freezing point of the pure solvent and the freezing point of the solution:

$$\Delta T_f = T_f^0 - T_f \tag{13.5.12}$$

where T_f^0 is the freezing point of the pure solvent and T_f is the freezing point of the solution.

The order of the terms is reversed compared with Equation $13.5.10$ to express the freezing point depression as a positive number. The relationship between ΔT_f and the solute concentration is given by an equation analogous to Equation $13.5.11$:

$$\Delta T_f = mK_f \tag{13.5.13}$$

where m is the molality of the solution and K_f is the molal freezing point depression constant for the solvent (in units of °C/m).

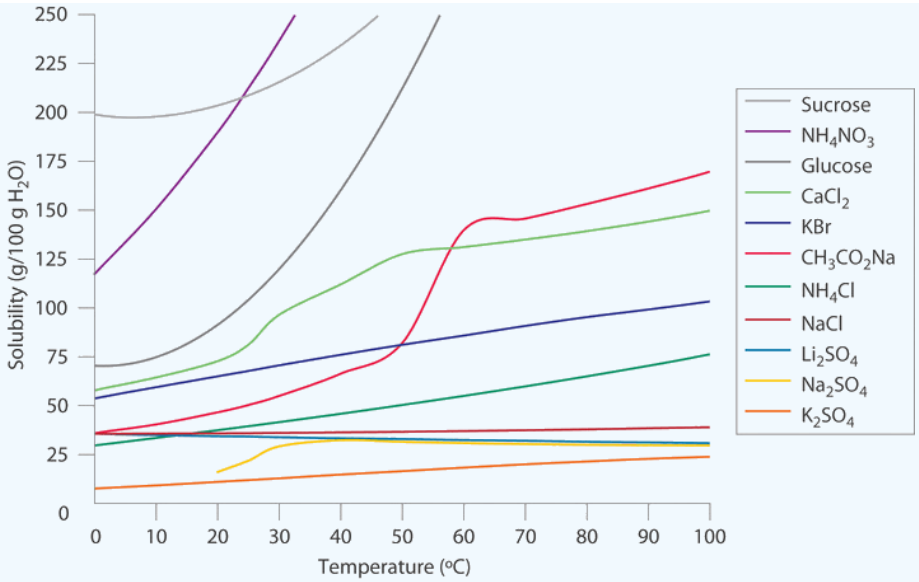
Like K_b, each solvent has a characteristic value of K_f (see Table $13.5.1$). Freezing point depression depends on the total number of dissolved nonvolatile solute particles, just as with boiling point elevation. Thus an aqueous NaCl solution has twice as large a freezing point depression as a glucose solution of the same molality.

People who live in cold climates use freezing point depression to their advantage in many ways. For example, salt is used to melt ice and snow on roads and sidewalks, ethylene glycol is added to engine coolant water to prevent an automobile engine from being destroyed, and methanol is added to windshield washer fluid to prevent the fluid from freezing.

> The decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus a pure liquid all depend on the total number of dissolved nonvolatile solute particles.

Example $13.5.4$: Salting the Roads

In colder regions of the United States, NaCl or $\mathrm{CaCl_2}$ is often sprinkled on icy roads in winter to melt the ice and make driving safer. Use the data in the Figure below to estimate the concentrations of two saturated solutions at 0°C, one of NaCl and one of $\mathrm{CaCl_2}$, and calculate the freezing points of both solutions to see which salt is likely to be more effective at melting ice.



Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds.

Graph of solubility against temperature. Plots of sucrose, NH4NO3, glucose, CaCl2, KBr, CH3CO2Na, NH4Cl, NaCl, Li2SO4, Na2SO4, K2SO4.

Given: solubilities of two compounds

Asked for: concentrations and freezing points

Strategy:

A. Estimate the solubility of each salt in 100 g of water from the figure. Determine the number of moles of each in 100 g and calculate the molalities.
B. Determine the concentrations of the dissolved salts in the solutions. Substitute these values into Equation 13.5.13 to calculate the freezing point depressions of the solutions.

Solution:

A From Figure above, we can estimate the solubilities of NaCl and $\mathrm{CaCl_2}$ to be about 36 g and 60 g, respectively, per 100 g of water at 0°C. The corresponding concentrations in molality are

$$m_{NaCl} = \left(\frac{36\ \cancel{g\ NaCl}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ NaCl}{58.44\ \cancel{g\ NaCl}}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.2\ m$$

$$m_{CaCl_2} = \left(\frac{60\ \cancel{g\ CaCl_2}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ CaCl_2}{110.98\ \cancel{g\ CaCl_2}}\right)\left(\frac{1000\ \cancel{g}}{1kg}\right) = 5.4\ m$$

The lower formula mass of NaCl more than compensates for its lower solubility, resulting in a saturated solution that has a slightly higher concentration than $CaCl_2$.

B Because these salts are ionic compounds that dissociate in water to yield two and three ions per formula unit of NaCl and $CaCl_2$, respectively, the actual concentrations of the dissolved species in the two saturated solutions are 2 × 6.2 m = 12 m for NaCl and 3 × 5.4 m = 16 m for $CaCl_2$. The resulting freezing point depressions can be calculated using Equation 13.5.13:

$$\mathrm{NaCl}: \Delta T_f = mK_f = (12\ \cancel{m})(1.86°C/\cancel{m}) = 22°C$$

$$\mathrm{CaCl_2}: \Delta T_f = mK_f = (16\ \cancel{m})(1.86°C/\cancel{m}) = 30°C$$

Because the freezing point of pure water is 0°C, the actual freezing points of the solutions are –22°C and –30°C, respectively. Note that $CaCl_2$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $CaCl_2$ is the salt usually sold for home use, and it is also often used on highways.

Because the solubilities of both salts decrease with decreasing temperature, the freezing point can be depressed by only a certain amount, regardless of how much salt is spread on an icy road. If the temperature is significantly below the minimum temperature at which one of these salts will cause ice to melt (say –35°C), there is no point in using salt until it gets warmer

Exercise 13.5.4

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Examples 13.5.5 and 13.5.5.

Answer available at the end of this section.

Example 13.5.5

Arrange these aqueous solutions in order of decreasing freezing points: 0.1 m KCl, 0.1 m glucose, 0.1 m SrCl2, 0.1 m ethylene glycol, 0.1 m benzoic acid, and 0.1 m HCl.

Given: molalities of six solutions

Asked for: relative freezing points

Strategy:

A. Identify each solute as a strong, weak, or nonelectrolyte, and use this information to determine the number of solute particles produced.
B. Multiply this number by the concentration of the solution to obtain the effective concentration of solute particles. The solution with the highest effective concentration of solute particles has the largest freezing point depression.

Solution:

A Because the molal concentrations of all six solutions are the same, we must focus on which of the substances are strong electrolytes, which are weak electrolytes, and which are nonelectrolytes to determine the actual numbers of particles in solution. KCl, $\mathrm{SrCl_2}$, and HCl are **strong electrolytes**, producing two, three, and two ions per formula unit, respectively. Benzoic acid is a weak electrolyte (approximately one particle per molecule), and glucose and ethylene glycol are both nonelectrolytes (one particle per molecule).

B The molalities of the solutions in terms of the total particles of solute are: KCl and HCl, 0.2 m; $SrCl_2$, 0.3 m; glucose and ethylene glycol, 0.1 m; and benzoic acid, 0.1–0.2 m. Because the magnitude of the decrease in freezing point is proportional to the concentration of dissolved particles, the order of freezing points of the solutions is: glucose and ethylene glycol (highest freezing point, smallest freezing point depression) > benzoic acid > HCl = KCl > $\mathrm{SrCl_2}$.

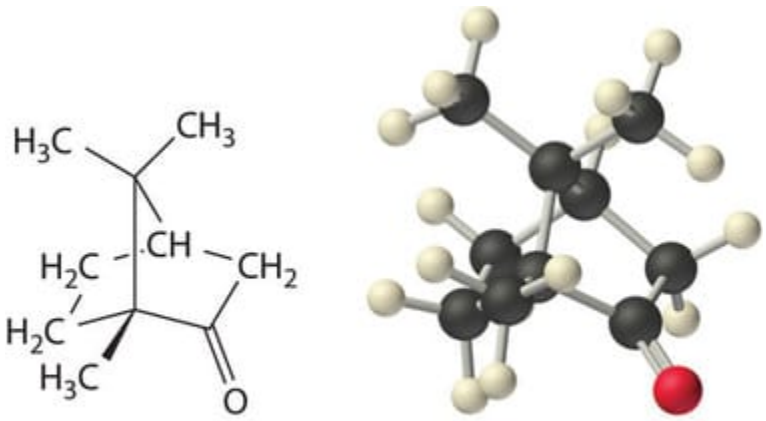
Exercise 13.5.5

Arrange these aqueous solutions in order of increasing freezing points: 0.2 m NaCl, 0.3 m acetic acid, 0.1 m $\mathrm{CaCl_2}$, and 0.2 m sucrose.

Answer available at the end of this section.

Colligative properties can also be used to determine the molar mass of an unknown compound. One method that can be carried out in the laboratory with minimal equipment is to measure the freezing point of a solution with a known mass of solute. This method is accurate for dilute solutions (≤1% by mass) because changes in the freezing point are usually large enough to measure

accurately and precisely. By comparing K_b and K_f values in Table 13.5.1, we see that changes in the boiling point are smaller than changes in the freezing point for a given solvent. Boiling point elevations are thus more difficult to measure precisely. For this reason, freezing point depression is more commonly used to determine molar mass than is boiling point elevation. Because of its very large value of K_f (37.8°C/m), d-(+)-camphor (Table 13.5.1) is often used to determine the molar mass of organic compounds by this method.



d-(+)-Camphor

Example 13.5.6: Sulfur

A 7.08 g sample of elemental sulfur is dissolved in 75.0 g of CS_2 to create a solution whose freezing point is –113.5°C. Use these data to calculate the molar mass of elemental sulfur and thus the formula of the dissolved S_n molecules (i.e., what is the value of n?).

Given: masses of solute and solvent and freezing point

Asked for: molar mass and number of S atoms per molecule

Strategy:

A. Use Equation 13.5.12, the measured freezing point of the solution, and the freezing point of CS_2 from Table 13.5.1 to calculate the freezing point depression. Then use Equation 13.5.13 and the value of K_f from Table 13.5.1 to calculate the molality of the solution.
B. From the calculated molality, determine the number of moles of solute present.
C. Use the mass and number of moles of the solute to calculate the molar mass of sulfur in solution. Divide the result by the molar mass of atomic sulfur to obtain n, the number of sulfur atoms per mole of dissolved sulfur.

Solution:

A The first step is to calculate the freezing point depression using Equation 13.5.12:

$$\Delta T_f = T_f^0 - T_f = -112.1°C - (-113.5°C) = 1.4°C$$

Then Equation 13.5.13 gives

$$m = \frac{\Delta T_f}{K_f} = \frac{1.4°\cancel{C}}{3.74°\cancel{C}/m} = 0.37\ m$$

B The total number of moles of solute present in the solution is

$$\text{moles solute} = \left(\frac{0.37 mol}{\cancel{kg}}\right)(75.0\ g)\left(\frac{1 kg}{1000\ g}\right) = 0.028\ mol$$

C We now know that 0.708 g of elemental sulfur corresponds to 0.028 mol of solute. The molar mass of dissolved sulfur is thus

$$\text{molar mass} = \frac{7.08\ g}{0.028\ mol} = 260\ g/mol$$

The molar mass of atomic sulfur is 32 g/mol, so there must be 260/32 = 8.1 sulfur atoms per mole, corresponding to a formula of S_8.

Exercise 13.5.6

One of the byproducts formed during the synthesis of C_{60} is a deep red solid containing only carbon. A solution of 205 mg of this compound in 10.0 g of CCl_4 has a freezing point of –23.38°C. What are the molar mass and most probable formula of the substance?

Answer available at the end of this section.

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Osmotic Pressure

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning “push”). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure 13.5.6, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the rate of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

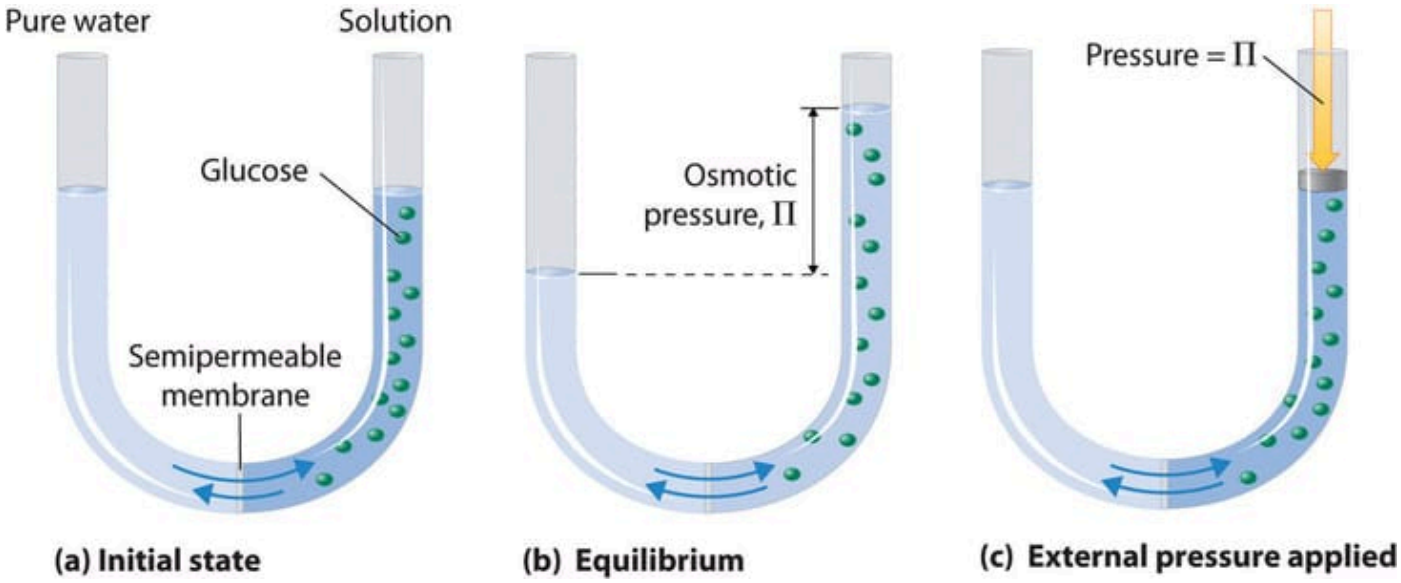


Figure 13.5.6: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.

Just as with any other colligative property, the osmotic pressure of a solution depends on the concentration of dissolved solute particles. Osmotic pressure obeys a law that resembles the ideal gas equation:

$$\Pi = \frac{nRT}{V} = MRT \tag{13.5.14}$$

where M is the number of moles of solute per unit volume of solution (i.e., the molarity of the solution), R is the ideal gas constant, and T is the absolute temperature.

As shown in Example 13.5.7, osmotic pressures tend to be quite high, even for rather dilute solutions.

Example 13.5.7

When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% NaCl by mass; the solution density is 1.02 g/mL at 25°C.

a. Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at 25°C.
b. If the normal osmotic pressure inside a yeast cell is 7.3 atm, corresponding to a total concentration of dissolved particles of 0.30 M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at 25°C?

Given: concentration, density, and temperature of NaCl solution; internal osmotic pressure of cell

Asked for: osmotic pressure of NaCl solution and concentration of glycerol needed

Strategy:

A. Calculate the molarity of the NaCl solution using the formula mass of the solute and the density of the solution. Then calculate the total concentration of dissolved particles.
B. Use Equation 13.5.14 to calculate the osmotic pressure of the solution.

C. Subtract the normal osmotic pressure of the cells from the osmotic pressure of the salt solution to obtain the additional pressure needed to balance the two. Use Equation 13.5.14 to calculate the molarity of glycerol needed to create this osmotic pressure.

Solution:

A The solution contains 4.0 g of NaCl per 100 g of solution. Using the formula mass of NaCl (58.44 g/mol) and the density of the solution (1.02 g/mL), we can calculate the molarity:

$$\begin{aligned} M_{NaCl} &= \frac{moles\ NaCl}{\text{liter solution}} \\ &= \left(\frac{4.0\ \cancel{g}\ NaCl}{58.44\ \cancel{g}/mol\ NaCl}\right)\left(\frac{1}{100\ \cancel{g\ solution}}\right)\left(\frac{1.02\ \cancel{g\ solution}}{1.00\ \cancel{mL}\ solution}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) \\ &= 0.70\ M\ \mathrm{NaCl} \end{aligned}$$

Because 1 mol of NaCl produces 2 mol of particles in solution, the total concentration of dissolved particles in the solution is (2)(0.70 M) = 1.4 M.

B Now we can use Equation 13.5.14 to calculate the osmotic pressure of the solution:

$$\begin{aligned} \Pi &= MRT \\ &= (1.4\ mol/L)\,[0.0821\ (L\cdot atm)/(K\cdot mol)]\,(298\ K) \\ &= 34\ atm \end{aligned}$$

C If the yeast cells are to exactly balance the external osmotic pressure, they must produce enough glycerol to give an additional internal pressure of (34 atm – 7.3 atm) = 27 atm. Glycerol is a nonelectrolyte, so we can solve Equation 13.5.14 for the molarity corresponding to this osmotic pressure:

$$\begin{aligned} M &= \frac{\Pi}{RT} \\ &= \frac{27\ \cancel{atm}}{[0.0821(L\cdot\cancel{atm})/(\cancel{K}\cdot mol)](298\ \cancel{K})} \\ &= 1.1\ M\ \text{glycerol} \end{aligned}$$

In solving this problem, we could also have recognized that the only way the osmotic pressures can be the same inside the cells and in the solution is if the concentrations of dissolved particles are the same. We are given that the normal concentration of dissolved particles in the cells is 0.3 M, and we have calculated that the NaCl solution is effectively 1.4 M in dissolved particles. The yeast cells must therefore synthesize enough glycerol to increase the internal concentration of dissolved particles from 0.3 M to 1.4 M—that is, an additional 1.1 M concentration of glycerol.

Exercise 13.5.7

Assume that the fluids inside a sausage are approximately 0.80 M in dissolved particles due to the salt and sodium nitrite used to prepare them. Calculate the osmotic pressure inside the sausage at 100°C to learn why experienced cooks pierce the semipermeable skin of sausages before boiling them.

Answer available at the end of this section.

Because of the large magnitude of osmotic pressures, osmosis is extraordinarily important in biochemistry, biology, and medicine. Virtually every barrier that separates an organism or cell from its environment acts like a semipermeable membrane, permitting the flow of water but not solutes. The same is true of the compartments inside an organism or cell. Some specialized barriers, such as those in your kidneys, are slightly more permeable and use a related process called dialysis, which permits both water and small molecules to pass through but not large molecules such as proteins.

The same principle has long been used to preserve fruits and their essential vitamins over the long winter. High concentrations

of sugar are used in jams and jellies not for sweetness alone but because they greatly increase the osmotic pressure. Thus any bacteria not killed in the cooking process are dehydrated, which keeps them from multiplying in an otherwise rich medium for bacterial growth. A similar process using salt prevents bacteria from growing in ham, bacon, salt pork, salt cod, and other preserved meats. The effect of osmotic pressure is dramatically illustrated in Figure 13.5.7, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.

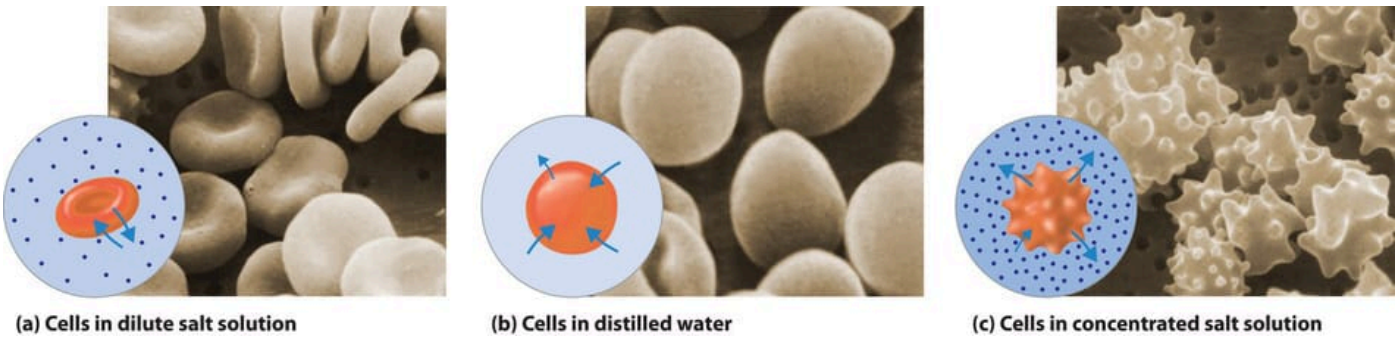


Figure 13.5.7: Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function.

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosis can be used to produce pure water from seawater. As shown schematically in Figure 13.5.8, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

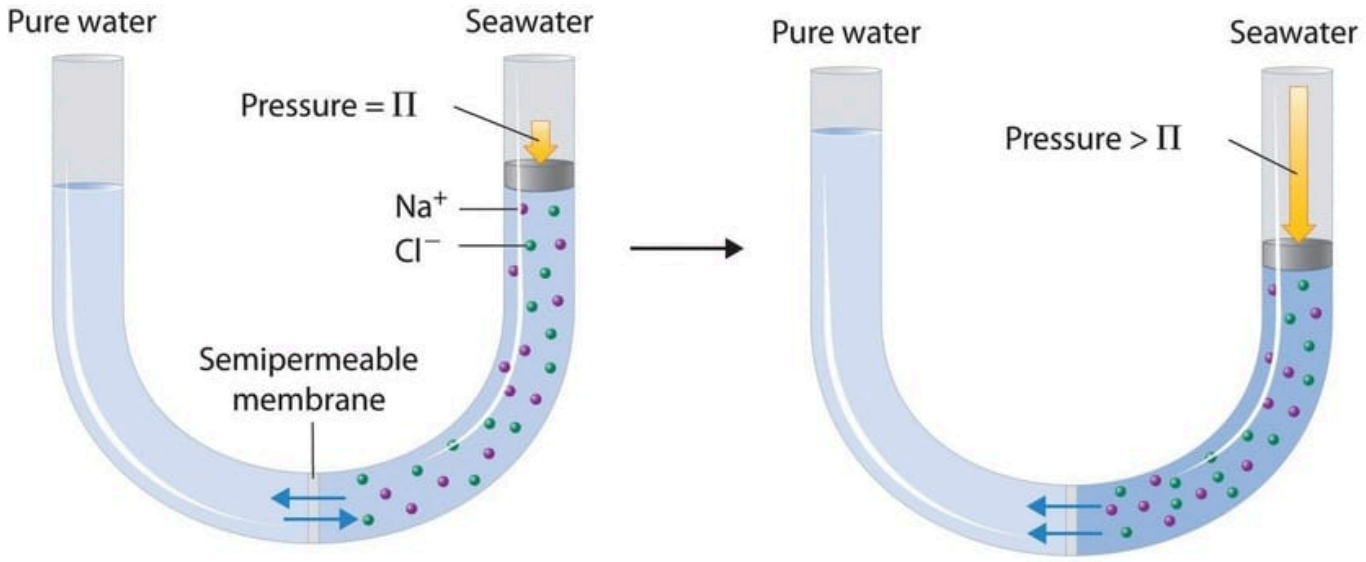


Figure 13.5.8: Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure (Π_{soln}), there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely.

YouTube Video

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A Video Discussing Osmotic Pressure. Video Link: Osmotic Pressure, YouTube(opens in new window) [youtu.be] (opens in new window)

Colligative Properties of Electrolyte Solutions

Thus far we have assumed that we could simply multiply the molar concentration of a solute by the number of ions per formula unit to obtain the actual concentration of dissolved particles in an electrolyte solution. We have used this simple model to predict such properties as freezing points, melting points, vapor pressure, and osmotic pressure. If this model were perfectly correct, we would expect the freezing point depression of a 0.10 m solution of sodium chloride, with 2 mol of ions per mole of NaCl in solution, to be exactly twice that of a 0.10 m solution of glucose, with only 1 mol of molecules per mole of glucose in solution. In reality, this is not always the case. Instead, the observed change in freezing points for 0.10 m aqueous solutions of NaCl and KCl are significantly less than expected (−0.348°C and −0.344°C, respectively, rather than −0.372°C), which suggests that fewer particles than we expected are present in solution.

The relationship between the actual number of moles of solute added to form a solution and the apparent number as determined by colligative properties is called the van't Hoff factor (i) and is defined as follows:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}} \tag{13.5.15}$$

Named for Jacobus Hendricus van't Hoff (1852–1911), a Dutch chemistry professor at the University of Amsterdam who won the first Nobel Prize in Chemistry (1901) for his work on thermodynamics and solutions.

As the solute concentration increases, the van't Hoff factor decreases.

The van't Hoff factor is therefore **a measure of a deviation from ideal behavior**. The lower the van't Hoff factor, the greater the deviation. As the data in Table $13.5.2$ show, the van't Hoff factors for ionic compounds are somewhat lower than expected; that is, their solutions apparently contain fewer particles than predicted by the number of ions per formula unit. As the concentration of the solute increases, the van't Hoff factor decreases because ionic compounds generally do not totally dissociate in aqueous solution.

Table $13.5.2$: van't Hoff Factors for 0.0500 M Aqueous Solutions of Selected Compounds at 25°C

Compound	i (measured)	i (ideal)
glucose	1.0	1.0
sucrose	1.0	1.0
$NaCl$	1.9	2.0
HCl	1.9	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0
$Ca(NO_3)_2$	2.5	3.0
$AlCl_3$	3.2	4.0
$MgSO_4$	1.4	2.0

Instead, some of the ions exist as ion pairs, a cation and an anion that for a brief time are associated with each other without an intervening shell of water molecules (Figure 13.5.9). Each of these temporary units behaves like a single dissolved particle until it dissociates. Highly charged ions such as Mg^{2+}, Al^{3+}, SO_4^{2-}, and PO_4^{3-} have a greater tendency to form ion pairs because of their strong electrostatic interactions. The actual number of solvated ions present in a solution can be determined by measuring a colligative property at several solute concentrations.

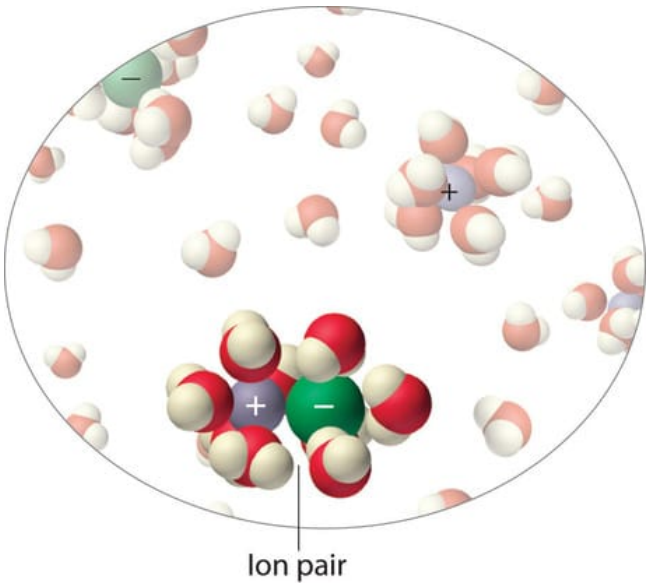


Figure 13.5.9: Ion Pairs. In concentrated solutions of electrolytes like $NaCl$, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles.

Example 13.5.8: Iron Chloride in Water

A 0.0500 M aqueous solution of $FeCl_3$ has an osmotic pressure of 4.15 atm at 25°C. Calculate the van't Hoff factor i for the solution.

Given: solute concentration, osmotic pressure, and temperature

Asked for: van't Hoff factor

Strategy:

A. Use Equation 13.5.14 to calculate the expected osmotic pressure of the solution based on the effective concentration of dissolved particles in the solvent.
B. Calculate the ratio of the observed osmotic pressure to the expected value. Multiply this number by the number of ions of solute per formula unit, and then use Equation 13.5.15 to calculate the van't Hoff factor.

Solution:

A If $\mathrm{FeCl_3}$ dissociated completely in aqueous solution, it would produce four ions per formula unit [Fe3+(aq) plus 3Cl–(aq)] for an effective concentration of dissolved particles of 4 × 0.0500 M = 0.200 M. The osmotic pressure would be

$$\begin{aligned}\Pi &= MRT \\ &= (0.200\ mol/L)\,[0.0821\ (L \cdot atm)/(K \cdot mol)]\,(298\ K) = 4.89\ atm\end{aligned}$$

B The observed osmotic pressure is only 4.15 atm, presumably due to ion pair formation. The ratio of the observed osmotic pressure to the calculated value is 4.15 atm/4.89 atm = 0.849, which indicates that the solution contains (0.849)(4) = 3.40 particles per mole of $\mathrm{FeCl_3}$ dissolved. Alternatively, we can calculate the observed particle concentration from the osmotic pressure of 4.15 atm:

$$4.15\ atm = M\left(\frac{0.0821\ (L \cdot atm)}{(K \cdot mol)}\right)(298\ K)$$

or after rearranging

$$M = 0.170 mol$$

The ratio of this value to the expected value of 0.200 M is 0.170 M/0.200 M = 0.850, which again gives us (0.850)(4) = 3.40 particles per mole of $\mathrm{FeCl_3}$ dissolved. From Equation 13.5.15, the van't Hoff factor for the solution is

$$i = \frac{3.40 \text{ particles observed}}{1 \text{ formula unit } \mathrm{FeCl_3}} = 3.40$$

Exercise 13.5.8: Magnesium Chloride in Water

Calculate the van't Hoff factor for a 0.050 m aqueous solution of $MgCl_2$ that has a measured freezing point of –0.25°C.

Answer available at the end of this section.

YouTube Video

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A Video Discussing the Colligative Properties in Solutions. Video Link: Colligative Properties in Solutions, YouTube(opens in new window) [youtu.be]

Summary

The colligative properties of a solution depend on only the total number of dissolved particles in solution, not on their chemical identity. Colligative properties include vapor pressure, boiling point, freezing point, and osmotic pressure. The addition of a nonvolatile solute (one without a measurable vapor pressure) decreases the vapor pressure of the solvent. The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as **Raoult's law**. Solutions that obey Raoult's law are called ideal solutions. Most real solutions exhibit positive or negative deviations from Raoult's law. The boiling point elevation (ΔT_b) and freezing point depression (ΔT_f) of a solution are defined as the differences between the boiling and freezing points, respectively, of the solution and the pure solvent. Both are proportional to the molality of the solute. When a solution and a pure solvent are separated by a semipermeable membrane, a barrier that allows solvent molecules but not solute molecules to pass through, the flow of solvent in opposing directions is unequal and produces an osmotic pressure, which is the difference in pressure between the two sides of the membrane. Osmosis is the net flow of solvent through such a membrane due to different solute concentrations. Dialysis uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through. In more concentrated solutions, or in solutions of salts with highly charged ions, the cations and anions can associate to form ion pairs, which decreases their effect on the colligative properties of the solution. The extent of ion pair formation is given by the van't Hoff factor (i), the ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt.

- **Henry's law:**

$$C = kP$$

- **Raoult's law**:

$$P_A = \chi_A P_A^0$$

- **vapor pressure lowering**:

$$P_A^0 - P_A = \Delta P_A = \chi_B P_A^0$$

- **vapor pressure of a system containing two volatile components**:

$$P_{tot} = \chi_A P_A^0 + (1 - \chi_A) P_B^0$$

- **boiling point elevation**:

$$\Delta T_b = mK_b$$

- **freezing point depression:**

$$\Delta T_f = mK_f$$

- **osmotic pressure**:

$$\Pi = nRTV = MRT$$

- **van 't Hoff factor**:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}}$$

Answers

Exercise 13.5.1

0.45 mmHg. This may seem like a small amount, but it constitutes about a 2% decrease in the vapor pressure of water and accounts in part for the higher humidity in the north-central United States near the Great Lakes, which are freshwater lakes. The decrease therefore has important implications for climate modeling.

Exercise 13.5.2

approximately equal

positive deviation (vapor pressure greater than predicted)

negative deviation (vapor pressure less than predicted)

Exercise 13.5.3

100.04°C, or 100°C to three significant figures. (Recall that 1 mol of NaCl produces 2 mol of dissolved particles. The small increase in temperature means that adding salt to the water used to cook pasta has essentially no effect on the cooking time.)

Exercise 13.5.4

–13.0°C

Exercise 13.5.5

0.2 m NaCl (lowest freezing point) < 0.3 m acetic acid ≈ 0.1 m $\mathrm{CaCl_2}$ < 0.2 m sucrose (highest freezing point)

Exercise 13.5.6

847 g/mol; $\mathrm{C_{70}}$

Exercise 13.5.7

24 atm

Exercise 13.5.8**: Magnesium Chloride in Water**

2.7 (versus an ideal value of 3).

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13.6: Colloids

Learning Objectives

- To distinguish between true solutions and solutions with aggregate particles.

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures. A suspension is a heterogeneous mixture of particles with diameters of about 1 µm (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloid is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions. The properties of suspensions, colloids, and solutions are summarized in Table 13.6.1.

Table 13.6.1: Properties of Liquid Solutions, Colloids, and Suspensions

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

Colloids and Suspensions

Colloids were first characterized in about 1860 by Thomas Graham, who also gave us Graham's law of diffusion and effusion. Although some substances, such as starch, gelatin, and glue, appear to dissolve in water to produce solutions, Graham found that they diffuse very slowly or not at all compared with solutions of substances such as salt and sugar. Graham coined the word colloid (from the Greek kólla, meaning "glue") to describe these substances, as well as the words sol and gel to describe certain types of colloids in which all of the solvent has been absorbed by the solid particles, thus preventing the mixture from flowing readily, as we see in Jell-O. Two other important types of colloids are aerosols, which are dispersions of solid or liquid particles in a gas, and emulsions, which are dispersions of one liquid in another liquid with which it is immiscible.

Colloids share many properties with solutions. For example, the particles in both are invisible without a powerful microscope, do not settle on standing, and pass through most filters. However, the particles in a colloid scatter a beam of visible light, a phenomenon known as the Tyndall effect,The effect is named after its discoverer, John Tyndall, an English physicist (1820–1893). whereas the particles of a solution do not. The Tyndall effect is responsible for the way the beams from automobile headlights are clearly visible from the side on a foggy night but cannot be seen from the side on a clear night. It is also responsible for the colored rays of light seen in many sunsets, where the sun's light is scattered by water droplets and dust particles high in the atmosphere. An example of the Tyndall effect is shown in Figure 13.6.1.



Figure 13.6.1: Tyndall Effect, the Scattering of Light by Colloids (CC BY; LibreTexts)

Although colloids and suspensions can have particles similar in size, the two differ in stability: the particles of a colloid remain dispersed indefinitely unless the temperature or chemical composition of the dispersing medium is changed. The chemical explanation for the stability of colloids depends on whether the colloidal particles are hydrophilic or hydrophobic.

Most proteins, including those responsible for the properties of gelatin and glue, are hydrophilic because their exterior surface is largely covered with polar or charged groups. Starch, a long-branched polymer of glucose molecules, is also hydrophilic. A hydrophilic colloid particle interacts strongly with water, resulting in a shell of tightly bound water molecules that prevents the particles from aggregating when they collide. Heating such a colloid can cause aggregation because the particles collide with greater energy and disrupt the protective shell of solvent. Moreover, heat causes protein structures to unfold, exposing previously buried hydrophobic groups that can now interact with other hydrophobic groups and cause the particles to aggregate and precipitate from solution. When an egg is boiled, for example, the egg white, which is primarily a colloidal suspension of a protein called albumin, unfolds and exposes its hydrophobic groups, which aggregate and cause the albumin to precipitate as a white solid.

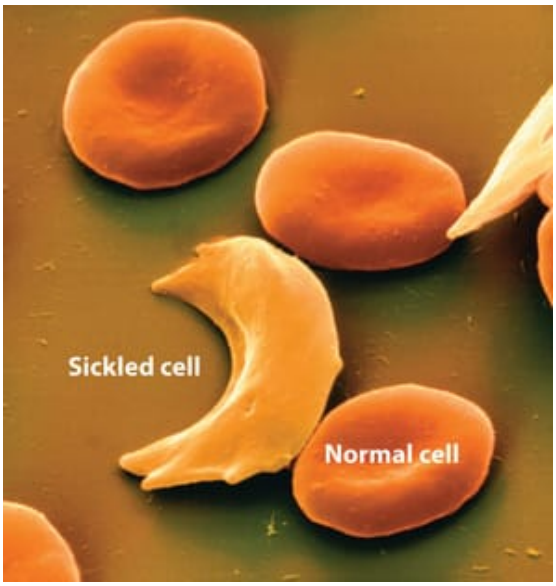


Figure 13.6.2: Sickle-Cell Anemia The characteristic shape of sickled red blood cells is the result of fibrous aggregation of hemoglobin molecules inside the cell.

A normal blood cell is circular in shape with a dimple in the middle, a sickled cell is banana shaped.

In some cases, a stable colloid can be transformed to an aggregated suspension by a minor chemical modification. Consider,

for example, the behavior of hemoglobin, a major component of red blood cells. Hemoglobin molecules normally form a colloidal suspension inside red blood cells, which typically have a “donut” shape and are easily deformed, allowing them to squeeze through the capillaries to deliver oxygen to tissues. In a common inherited disease called sickle-cell anemia, one of the amino acids in hemoglobin that has a hydrophilic carboxylic acid side chain (glutamate) is replaced by another amino acid that has a hydrophobic side chain (valine). Under some conditions, the abnormal hemoglobin molecules can aggregate to form long, rigid fibers that cause the red blood cells to deform, adopting a characteristic sickle shape that prevents them from passing through the capillaries (Figure 13.6.2). The reduction in blood flow results in severe cramps, swollen joints, and liver damage. Until recently, many patients with sickle-cell anemia died before the age of 30 from infection, blood clots, or heart or kidney failure, although individuals with the sickle-cell genetic trait are more resistant to malaria than are those with “normal” hemoglobin.

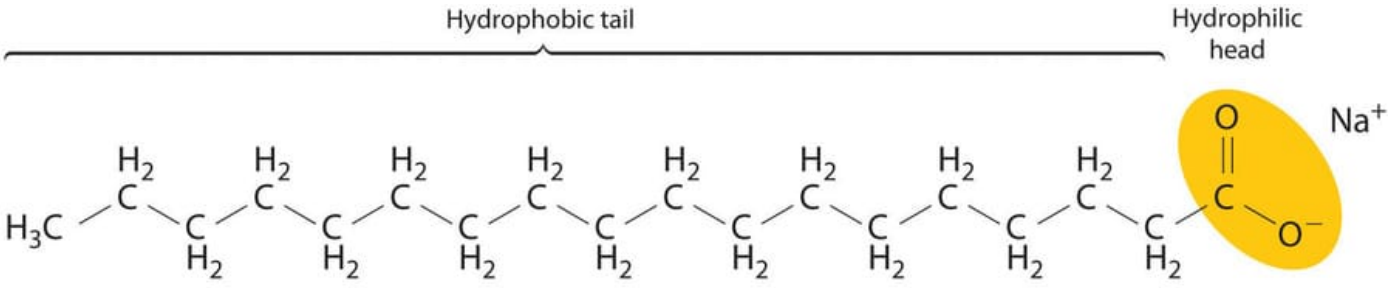


Figure 13.6.3: Formation of New Land by the Destabilization of a Colloid Suspension. This satellite photograph shows the Mississippi River delta from New Orleans (top) to the Gulf of Mexico (bottom). Where seawater mixes with freshwater from the Mississippi River, colloidal clay particles in the river water precipitate (tan area).

Aggregation and precipitation can also result when the outer, charged layer of a particle is neutralized by ions with the opposite charge. In inland waterways, clay particles, which have a charged surface, form a colloidal suspension. High salt concentrations in seawater neutralize the charge on the particles, causing them to precipitate and form land at the mouths of large rivers, as seen in the satellite view in Figure 13.6.3. Charge neutralization is also an important strategy for precipitating solid particles from gaseous colloids such as smoke, and it is widely used to reduce particulate emissions from power plants that burn fossil fuels.

Emulsions

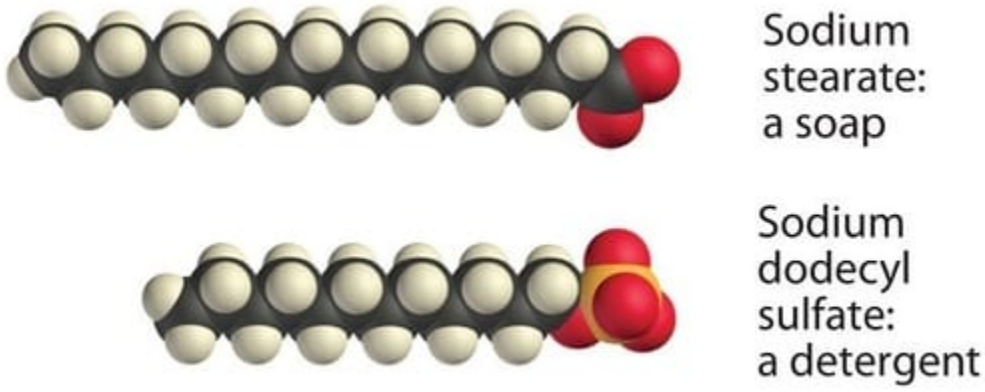
Emulsions are colloids formed by the dispersion of a hydrophobic liquid in water, thereby bringing two mutually insoluble liquids, such as oil and water, in close contact. Various agents have been developed to stabilize emulsions, the most successful being molecules that combine a relatively long hydrophobic “tail” with a hydrophilic “head”:



Sodium stearate: a soap

Bond line drawing of soap, The hydrophobic tail is a long hydrocarbon chain. The hydrophilic heat is a carbon double bonded to an oxygen and single bonded to a negatively charged oxygen.

Examples of such emulsifying agents include soaps, which are salts of long-chain carboxylic acids, such as sodium stearate $[CH_3(CH_2)_{16}CO_2{-}Na^+]$, and detergents, such as sodium dodecyl sulfate $[CH_3(CH_2)_{11}OSO_3{-}Na^+]$, whose structures are as follows:



When you wash your laundry, the hydrophobic tails of soaps and detergents interact with hydrophobic particles of dirt or grease through dispersion forces, dissolving in the interior of the hydrophobic particle. The hydrophilic group is then exposed at the surface of the particle, which enables it to interact with water through ion–dipole forces and hydrogen bonding. This causes the particles of dirt or grease to disperse in the wash water and allows them to be removed by rinsing. Similar agents are used in the food industry to stabilize emulsions such as mayonnaise.

A related mechanism allows us to absorb and digest the fats in buttered popcorn and French fries. To solubilize the fats so that they can be absorbed, the gall bladder secretes a fluid called bile into the small intestine. Bile contains a variety of bile salts, detergent-like molecules that emulsify the fats.

Micelles

Detergents and soaps are surprisingly soluble in water in spite of their hydrophobic tails. The reason for their solubility is that they do not, in fact, form simple solutions. Instead, above a certain concentration they spontaneously form micelles, which are spherical or cylindrical aggregates that minimize contact between the hydrophobic tails and water. In a micelle, only the hydrophilic heads are in direct contact with water, and the hydrophobic tails are in the interior of the aggregate (Figure $13.6.4a$).

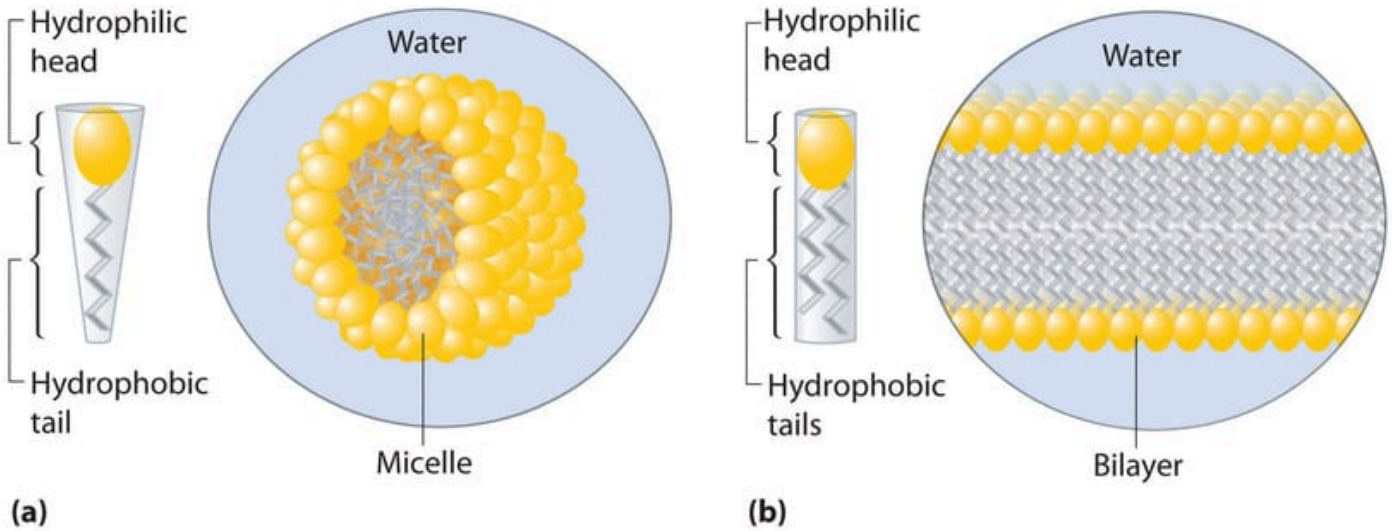
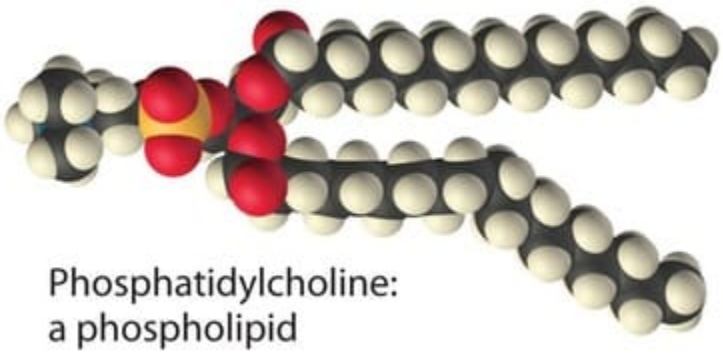


Figure $13.6.4$: Micelles and a Phospholipid Bilayer. (a) Soaps and detergents, which contain a single hydrophobic tail on each molecule, form spherical micelles with the intertwined tails in the interior and the hydrophilic head groups on the exterior. (b) Phospholipids, which have two hydrophobic tails, tend to form extended double layers in which the hydrophobic tails are sandwiched between the hydrophilic head groups.

A large class of biological molecules called phospholipids consists of detergent-like molecules with a hydrophilic head and two hydrophobic tails, as can be seen in the molecule of phosphatidylcholine. The additional tail results in a cylindrical shape that

prevents phospholipids from forming a spherical micelle. Consequently, phospholipids form bilayers, extended sheets consisting of a double layer of molecules. As shown in Figure $13.6.4b$, the hydrophobic tails are in the center of the bilayer, where they are not in contact with water, and the hydrophilic heads are on the two surfaces, in contact with the surrounding aqueous solution.



A cell membrane is essentially a mixture of phospholipids that form a phospholipid bilayer. One definition of a cell is a collection of molecules surrounded by a phospholipid bilayer that is capable of reproducing itself. The simplest cells are bacteria, which consist of only a single compartment surrounded by a single membrane. Animal and plant cells are much more complex, however, and contain many different kinds of compartments, each surrounded by a membrane and able to carry out specialized tasks.

Summary

A suspension is a heterogeneous mixture of particles of one substance distributed throughout a second phase; the dispersed particles separate from the dispersing phase on standing. In contrast, the particles in a colloid are smaller and do not separate on standing. A colloid can be classified as a sol, a dispersion of solid particles in a liquid or solid; a gel, a semisolid sol in which all of the liquid phase has been absorbed by the solid particles; an aerosol, a dispersion of solid or liquid particles in a gas; or an emulsion, a dispersion of one liquid phase in another. A colloid can be distinguished from a true solution by its ability to scatter a beam of light, known as the Tyndall effect. Hydrophilic colloids contain an outer shell of groups that interact favorably with water, whereas hydrophobic colloids have an outer surface with little affinity for water. Emulsions are prepared by dispersing a hydrophobic liquid in water. In the absence of a dispersed hydrophobic liquid phase, solutions of detergents in water form organized spherical aggregates called micelles. Phospholipids are a class of detergent-like molecules that have two hydrophobic tails attached to a hydrophilic head. A bilayer is a two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail with a hydrophobic interior and a hydrophilic exterior. Cells are collections of molecules that are surrounded by a phospholipid bilayer called a cell membrane and are able to reproduce themselves.

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13.E: Properties of Solutions (Exercises)

13.1: The Solution Process

Conceptual Problems

1. Classify each of the following as a heterogeneous mixture or homogeneous mixture. Explain your rationale in each case.
   a. aqueous ammonia
   b. liquid decongestant
   c. vinegar
   d. seawater
   e. gasoline
   f. fog
2. Solutions and heterogeneous mixtures are at the extreme ends of the solubility scale. Name one type of mixture that is intermediate on this scale. How are the properties of the mixture you have chosen different from those of a solution or a heterogeneous mixture?

   a. a naphthalene mothball dissolving in benzene
   b. a sample of a common drain cleaner that has a mixture of $NaOH$ crystals and Al chunks dissolving in water to give H_2 gas and an aqueous solution of Na^+, OH^-, and Al^{3+} ions
   c. an iron ship anchor slowly dissolving in seawater
   d. sodium metal dissolving in liquid ammonia
   e. a sugar cube dissolving in a cup of hot tea
   f. SO_3 gas dissolving in water to produce sulfuric acid
   g. calcium oxide dissolving in water to produce a basic solution
   h. metallic gold dissolving in a small quantity of liquid mercury

3. Classify each process as simple dissolution or a chemical reaction.
4. Classify each process as simple dissolution or a chemical reaction.
5. You notice that a gas is evolved as you are dissolving a solid in a liquid. Will you be able to recover your original solid by evaporation? Why or why not?
6. Why is heat evolved when sodium hydroxide pellets are dissolved in water? Does this process correspond to simple dissolution or a chemical reaction? Justify your answer.
7. Which process(es) is the simple formation of a solution, and which process(es) involves a chemical reaction?

   a. mixing an aqueous solution of NaOH with an aqueous solution of HCl
   b. bubbling HCl gas through water
   c. adding iodine crystals to CCl_4
   d. adding sodium metal to ethanol to produce sodium ethoxide ($C_2H_5O^-Na^+$) and hydrogen gas

8. Using thermochemical arguments, explain why some substances that do not form a solution at room temperature will form a solution when heated. Explain why a solution can form even when ΔH_{soln} is positive.
9. If you wanted to formulate a new compound that could be used in an instant cold pack, would you select a compound with a positive or negative value of ΔH_{soln} in water? Justify your answer.
10. Why is entropy the dominant factor in the formation of solutions of two or more gases? Is it possible for two gases to be immiscible? Why or why not?

Conceptual Answers

1. Homogeneous mixtures: aqueous ammonia, liquid decongestant, vinegar, and gasoline. Heterogeneous mixtures: seawater and fog.
2. All are chemical reactions except dissolving iodine crystals in CCl_4.

13.2: Saturated Solutions and Solubility

Conceptual Problems

1. If a compound is only slightly soluble in a particular solvent, what are the relative strengths of the solvent–solvent and solute–solute interactions versus the solute–solvent interactions?
2. Predict whether each of the following sets of conditions favors formation of a solution:

Intermolecular Attractive Forces (Solute)	Intermolecular Attractive Forces (Solvent)	ΔH_{soln}
London dispersion	hydrogen bonding	slightly positive
dipole–dipole	hydrogen bonding	very negative
ionic	dipole–dipole	slightly positive
ionic	London dispersion	positive

3. Arrange the following liquids in order of increasing solubility in water: t-butanol [(CH3)3COH], benzene, ammonia, and heptane. Justify your answer.
4. Which compound in each pair will be more soluble in water? Explain your reasoning in each case.
   a. toluene (C_7H_8) or ethyl ether ($C_2H_5OC_2H_5$)
   b. chloroform ($CHCl_3$) or acetone (CH_3COCH_3)
   c. carbon tetrachloride (CCl_4) or tetrahydrofuran (C_4H_8O)
   d. $CaCl_2$ or CH_2Cl_2
5. Which compound in each pair will be more soluble in benzene? Explain your reasoning in each case.
   a. cyclohexane or methanol
   b. I_2 or $MgCl_2$
   c. methylene chloride (CH_2Cl_2) or acetic acid
6. Two water-insoluble compounds—n-decylamine $[CH_3(CH_2)_9NH_2]$ and n-decane—can be separated by the following procedure: The compounds are dissolved in a solvent such as toluene that is immiscible with water. When adding an aqueous HCl solution to the mixture and stirring vigorously, the HCl reacts with one of the compounds to produce a salt. When the stirring is stopped and the mixture is allowed to stand, two layers are formed. At this point, each layer contains only one of the two original compounds. After the layers are separated, adding aqueous $NaOH$ to the aqueous layer liberates one of the original compounds, which can then be removed by stirring with a second portion of toluene to extract it from the water.
   a. Identify the compound that is present in each layer following the addition of HCl. Explain your reasoning.
   b. How can the original compounds be recovered from the toluene solution?
7. Bromine and iodine are both soluble in CCl_4, but bromine is much more soluble. Why?
8. A solution is made by mixing 50.0 mL of liquid A with 75.0 mL of liquid B. Which is the solute, and which is the solvent? Is it valid to assume that the volume of the resulting solution will be 125 mL? Explain your answer.
9. The compounds NaI, NaBr, and NaCl are far more soluble in water than NaF, a substance that is used to fluoridate drinking water. In fact, at 25°C the solubility of NaI is 184 g/100 mL of water, versus only 4.2 g/100 mL of water for NaF. Why is sodium iodide so much more soluble in water? Do you expect KCl to be more soluble or less soluble in water than NaCl?
10. When water is mixed with a solvent with which it is immiscible, the two liquids usually form two separate layers. If the density of the nonaqueous solvent is 1.75 g/mL at room temperature, sketch the appearance of the heterogeneous mixture in a beaker and label which layer is which. If you were not sure of the density and the identity of the other liquid, how might you be able to identify which is the aqueous layer?
11. When two liquids are immiscible, the addition of a third liquid can occasionally be used to induce the formation of a homogeneous solution containing all three.
    a. Ethylene glycol ($HOCH_2CH_2OH$) and hexane are immiscible, but adding acetone $[(CH_3)_2CO]$ produces a homogeneous solution. Why does adding a third solvent produce a homogeneous solution?
    b. Methanol and n-hexane are immiscible. Which of the following solvents would you add to create a homogeneous solution—water, n-butanol, or cyclohexane? Justify your choice.
12. Some proponents of vitamin therapy for combating illness encourage the consumption of large amounts of fat-soluble vitamins. Why can this be dangerous? Would it be as dangerous to consume large amounts of water-soluble vitamins? Why or why not?
13. Why are most metals insoluble in virtually all solvents?

14. Because sodium reacts violently with water, it is difficult to weigh out small quantities of sodium metal for a reaction due to its rapid reaction with small amounts of moisture in the air. Would a Na/Hg amalgam be as sensitive to moisture as metallic sodium? Why or why not? A Na/K alloy is a liquid at room temperature. Will it be more or less sensitive to moisture than solid Na or K?
15. Dental amalgams often contain high concentrations of Hg, which is highly toxic. Why isn't dental amalgam toxic?
16. Arrange 2,2,3-trimethylpentane, 1-propanol, toluene (C_7H_8), and dimethyl sulfoxide [$(CH_3)_2S{=}O$] in order of increasing dipole moment. Explain your reasoning.
17. Arrange acetone, chloroform, cyclohexane, and 2-butanol in order of increasing dielectric constant. Explain your reasoning.
18. Dissolving a white crystalline compound in ethanol gave a blue solution. Evaporating the ethanol from the solution gave a bluish-crystalline product, which slowly transformed into the original white solid on standing in the air for several days. Explain what happened. How does the mass of the initial bluish solid compare with the mass of the white solid finally recovered?
19. You have been asked to develop a new drug that could be used to bind Fe3+ ions in patients who suffer from iron toxicity, allowing the bound iron to be excreted in the urine. Would you consider a crown ether or a cryptand to be a reasonable candidate for such a drug? Explain your answer.
20. Describe two different situations in which fractional crystallization will not work as a separation technique when attempting to isolate a single compound from a mixture.
21. You have been given a mixture of two compounds—A and B—and have been told to isolate pure A. You know that pure A has a lower solubility than pure B and that the solubilities of both A and B increase with temperature. Outline a procedure to isolate pure A. If B had the lower solubility, could you use the same procedure to isolate pure A? Why or why not?

Conceptual Answers

7. London dispersion forces increase with increasing atomic mass. Iodine is a solid while bromine is a liquid due to the greater intermolecular interactions between the heavier iodine atoms. Iodine is less soluble than bromine in virtually all solvents because it requires more energy to separate I_2 molecules than Br_2 molecules.

11.

a. A third solvent with intermediate polarity and/or dielectric constant can effectively dissolve both of the immiscible solvents, creating a single liquid phase.
b. n-butanol—it is intermediate in polarity between methanol and n-hexane, while water is more polar than either and cyclohexane is comparable to n-hexane.

15. In dental amalgam, the mercury atoms are locked in a solid phase that does not undergo corrosion under physiological conditions; hence, the mercury atoms cannot readily diffuse to the surface where they could vaporize or undergo chemical reaction.

21. Dissolve the mixture of A and B in a solvent in which they are both soluble when hot and relatively insoluble when cold, filter off any undissolved B, and cool slowly. Pure A should crystallize, while B stays in solution. If B were less soluble, it would be impossible to obtain pure A by this method in a single step, because some of the less soluble compound (B) will always be present in the solid that crystallizes from solution.

13.3: Factors Affecting Solubility

Conceptual Problems

1. Use the kinetic molecular theory of gases discussed in Chapter 10 to explain why the solubility of virtually all gases in liquids decreases with increasing temperature.
2. An industrial plant uses water from a nearby stream to cool its reactor and returns the water to the stream after use. Over a period of time, dead fish start to appear downstream from the plant, but there is no evidence for any leaks of potentially toxic chemicals into the stream. What other factor might be causing the fish to die?
3. One manufacturer's instructions for setting up an aquarium specify that if boiled water is used, the water must be cooled to room temperature and allowed to stand overnight before fish are added. Why is it necessary for the water to stand?
4. Using a carbonated beverage as an example, discuss the effect of temperature on the "fizz." How does the "foaminess" of a carbonated beverage differ between Los Angeles, California, and Denver, Colorado?
5. A common laboratory technique for degassing a solvent is to place it in a flask that is sealed to the atmosphere and then

evacuate the flask to remove any gases above the liquid. Why is this procedure effective? Why does the temperature of the solvent usually decrease substantially during this process?

Conceptual Answers

3. When water is boiled, all of the dissolved oxygen and nitrogen are removed. When the water is cooled to room temperature, it initially contains very little dissolved oxygen. Allowing the water to stand overnight allows oxygen in the air to dissolve, so that the fish will not suffocate.

5. Evacuating the flask to remove gases decreases the partial pressure of oxygen above the solution. According to Henry's law, the solubility of any gas decreases as its partial pressure above the solution decreases. Consequently, dissolved oxygen escapes from solution into the gas phase, where it is removed by the vacuum pump. Filling the flask with nitrogen gas and repeating this process several times effectively removes almost all of the dissolved oxygen. The temperature of the solvent decreases because some solvent evaporates as well during this process. The heat that is required to evaporate some of the liquid is initially removed from the rest of the solvent, decreasing its temperature.

Numerical Problems

1. The solubility of CO_2 in water at 0°C and 1 atm is 0.335 g/100 g of H_2O. At 20°C and 1 atm, the solubility of CO_2 in water is 0.169 g/100 g of H_2O.
   a. What volume of CO_2 would be released by warming 750 g of water saturated with CO_2 from 0°C to 20°C?
   b. What is the value of the Henry's law constant for CO_2 under each set of conditions?

2. The solubility of O_2 in 100 g of H_2O at varying temperatures and a pressure of 1 atm is given in the following table:

Solubility (g)	Temperature (°C)
0.0069	0
0.0054	10
0.0043	20

a. What is the value of the Henry's law constant at each temperature?
b. Does Henry's law constant increase or decrease with increasing temperature?
c. At what partial pressure of O_2 would the concentration of O_2 in water at 0°C be the same as the concentration in water at 20°C at a partial pressure of 1 atm?
d. Assuming that air is 20% O_2 by volume, at what atmospheric pressure would the O_2 concentration be the same at 20°C as it is at atmospheric pressure and 0°C?

Numerical Answer

1. a. 0.678 L CO_2
   b. $k_{0°C} = 7.61 \times 10^{-2}\ M/atm$, $k_{20°C} = 3.84 \times 10^{-2}\ M/atm$

13.4: Ways of Expressing Concentration

Conceptual Problems

1. Does the molality have the same numerical value as the molarity for a highly concentrated aqueous solution of fructose ($C_6H_{12}O_6$) (approximately 3.2 M)? Why or why not?
2. Explain why the molality and molarity of an aqueous solution are not always numerically identical. Will the difference between the two be greater for a dilute or a concentrated solution? Explain your answer.
3. Under what conditions are molality and molarity likely to be equal? Is the difference between the two greater when water is the solvent or when the solvent is not water? Why?
4. What is the key difference between using mole fraction or molality versus molarity to describe the concentration of a

solution? Which unit(s) of concentration is most appropriate for experiments that must be carried out at several different temperatures?

5. An experiment that relies on very strict control of the reaction stoichiometry calls for adding 50.0 mL of a 0.95 M solution of A to 225 mL of a 1.01 M solution of B, followed by heating for 1 h at 60°C. To save time, a student decided to heat solution B to 60°C before measuring out 225 mL of solution B, transferring it to the flask containing solution A, and proceeding normally. This change in procedure caused the yield of product to be less than usual. How could such an apparently minor change in procedure have resulted in a decrease in the yield?

Numerical Problems

1. Complete the following table for aqueous solutions of the compounds given.

Compound	Molarity (M)	Solution Density (g/mL)	Mole Fraction (X)
H_2SO_4	18.0	1.84	
CH_3COOH		1.00	7.21×10^{-3}
KOH	3.60	1.16	

2. Complete the following table for each compound given.

Compound	Mass (g)	Volume of Solution (mL)	Molarity (M)
Na_2SO_4	7.80	225	
KNO_3		125	1.27
NaO_2CCH_3	18.64		0.95

3. How would you prepare 100.0 mL of an aqueous solution with 0.40 M KI? a solution with 0.65 M $NaCN$?
4. Calculate the molality of a solution with 775 mg of $NaCl$ in 500.0 g of water. Do you expect the molarity to be the same as the molality? Why or why not?
5. What is the molarity of each solution?

    a. 12.8 g of glucose ($C_6H_{12}O_6$) in water, total volume 150.0 mL
    b. 9.2 g of Na_3PO_4 in water, total volume 200.0 mL
    c. 843 mg of I2 in $EtOH$, total volume 150.0 mL

6. A medication used to treat abnormal heart rhythms is labeled “Procainamide 0.5 g/250 cc.” Express this concentration in parts per thousand.
7. Meperidine is a medication used for pain relief. A bottle of meperidine is labeled as 50 mg/mL. Express this concentration in parts per thousand.
8. An aqueous solution that is 4.61% NaOH by mass has a density of 1.06 g/mL. Calculate the molarity of the solution, the mole fraction of $NaOH$, and the molality of the solution.
9. A solution of concentrated phosphoric acid contains 85.0% H_3PO_4 by mass and has a density of 1.684 g/mL. Calculate the following.

    a. the molarity of the solution
    b. the mole fraction of H_3PO_4
    c. the molality of the solution

10. A solution of commercial concentrated nitric acid is 16 M $HNO3$ and has a density of 1.42 g/mL. What is the percentage of $HNO3$ in the solution by mass? What is the molality?
11. A commercial aqueous ammonia solution contains 28.0% $NH3$ by mass and has a density of 0.899 g/mL. Calculate the following.
    a. the molarity
    b. the mole fraction
12. Concentrated, or glacial, acetic acid is pure acetic acid and has a density of 1.053 g/mL. It is widely used in organic syntheses, in the manufacture of rayon and plastics, as a preservative in foods, and occasionally to treat warts. What volume

of glacial acetic acid is required to prepare 5.00 L of a 1.75 M solution of acetic acid in ethanol?

13. Solutions of sodium carbonate decahydrate, also known as washing soda, are used as skin cleansers. The solubility of this compound in cold water is 21.52 g/100 mL. If a saturated solution has a density of 1.20 g/mL, what is its molarity? What is the mole fraction of sodium carbonate decahydrate in this solution?
14. Hydrogen peroxide (H_2O_2) is usually sold over the counter as an aqueous solution that is 3% by mass. Assuming a solution density of 1.01 g/mL, what is the molarity of hydrogen peroxide? What is the molar concentration of a solution that is 30% hydrogen peroxide by mass (density = 1.112 g/mL)? How would you prepare 100.0 mL of a 3% solution from the 30% solution?
15. Determine the concentration of a solution with 825 mg of Na_2HPO_4 dissolved in 450.0 mL of H_2O at 20°C in molarity, molality, mole fraction, and parts per million. Assume that the density of the solution is the same as that of water. Which unit of concentration is most convenient for calculating vapor pressure changes? Why?
16. How many moles of Cl^- are there in 25.0 mL of a 0.15 M $CaCl_2$ solution?
17. How many moles of Na+ are there in 25.0 g of a $1.33 \times 10^{-3}\ m\ Na_2HPO_4$ solution? What is the sodium concentration of this solution in ppb?
18. How many grams of copper are there in 30.0 mL of a 0.100 M $CuSO_4$ solution?
19. How many grams of nitrate ion are there in 75.0 g of a $1.75 \times 10^{-4} m\ Pb(NO_3)_2$ solution? What is the nitrate concentration of the solution in ppb?
20. How many milliliters of a 0.750 M solution of K_2CrO_4 are required to deliver 250 mg of chromate ion?
21. How many milliliters of a $1.95 \times 10^{-6} M$ solution of Ag_3PO_4 are required to deliver 14.0 mg of Ag^+?
22. Iron reacts with bromine according to the following equation:

$$2Fe_{(s)} + 3Br_{2(aq)} \rightarrow 2FeBr_{3(aq)} \tag{13.E.1}$$

23. How many milliliters of a $5.0 \times 10^{-2} M$ solution of bromine in water are required to react completely with 750.0 mg of iron metal?
24. Aluminum reacts with HCl according to the following equation:

$$2Al_{(s)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 3H_{2(g)} \tag{13.E.2}$$

25. If 25.0 mL of a solution of HCl in water is required to react completely with 1.05 g of aluminum metal, what is the molarity of the HCl solution?
26. The precipitation of silver chloride is a diagnostic test for the presence of chloride ion. If 25.0 mL of 0.175 M $AgNO_3$ are required to completely precipitate the chloride ions from 10.0 mL of an $NaCl$ solution, what was the original concentration of $NaCl$?
27. Barium sulfate is virtually insoluble. If a 10.0 mL solution of 0.333 M $Ba(NO_3)_2$ is stirred with 40.0 mL of a 0.100 M Na_2SO_4 , how many grams of barium sulfate will precipitate? Which reactant is present in excess? What is its final concentration?

13.5: Colligative Properties

Conceptual Problems

1. Why does the vapor pressure of a solvent decrease when adding a nonvolatile solute?
2. Does seawater boil at the same temperature as distilled water? If not, which has the higher boiling point? Explain your answer.
3. Which will be more soluble in benzene—O_2 or HCl? Will H_2S or HCl be more soluble in water? Explain your reasoning in each case.
4. Will the vapor pressure of a solution of hexane and heptane have an ideal vapor pressure curve (i.e., obey Raoult's law)? Explain your answer. What properties of two liquids determine whether a solution of the two will exhibit an ideal behavior?
5. Predict whether the following mixtures will exhibit negative, zero, or positive deviations from Raoult's law. Explain your reasoning in each case.
   - carbon tetrachloride and heptane
   - methanol and tetrahydrofuran (C4H8O)
   - acetone [(CH3)2C=CO] and dichloromethane
   - hexane and methanol
6. Why are deviations from the ideal behavior predicted by Raoult's law more common for solutions of liquids than are deviations from the ideal behavior predicted by the ideal gas law for solutions of gases?
7. Boiling point elevation is proportional to the molal concentration of the solute. Is it also proportional to the molar

concentration of the solution? Why or why not?

8. Many packaged foods in sealed bags are cooked by placing the bag in boiling water. How could you reduce the time required to cook the contents of the bag using this cooking method?
9. If the costs per kilogram of ethylene glycol and of ethanol were the same, which would be the more cost-effective antifreeze?
10. Many people get thirsty after eating foods such as ice cream or potato chips that have a high sugar or salt content, respectively. Suggest an explanation for this phenomenon.
11. When two aqueous solutions with identical concentrations are separated by a semipermeable membrane, no net movement of water occurs. What happens when a solute that cannot penetrate the membrane is added to one of the solutions? Why?
12. A solution injected into blood vessels must have an electrolyte concentration nearly identical to that found in blood plasma. Why? What would happen if red blood cells were placed in distilled water? What would happen to red blood cells if they were placed in a solution that had twice the electrolyte concentration of blood plasma?
13. If you were stranded on a desert island, why would drinking seawater lead to an increased rate of dehydration, eventually causing you to die of thirst?
14. What is the relationship between the van't Hoff factor for a compound and its lattice energy?

Numerical Problems

1. Hemoglobin is the protein that is responsible for the red color of blood and for transporting oxygen from the lungs to the tissues. A solution with 11.2 mg of hemoglobin per mL has an osmotic pressure of 2.9 mmHg at 5°C. What is the molecular mass of hemoglobin?
2. To determine the molar mass of the antifreeze protein from the Arctic right-eye flounder, the osmotic pressure of a solution containing 13.2 mg of protein per mL was measured and found to be 21.2 mmHg at 10°C. What is the molar mass of the protein?
3. What is the osmotic pressure at 21.0°C of 13.5 mL of a solution with 1.77 g of sucrose (\)C_{12}H_{22}O_{11})\)? A solution of $NaNO_3$ is generated by dissolving 1.25 g of NaNO3 in enough water to give a final volume of 25.0 mL. What is the osmotic pressure of this sample at 25.0°C?
4. Which would have the lower vapor pressure—an aqueous solution that is 0.12 M in glucose or one that is 0.12 M in $CaCl_2$? Why?
5. What is the total particle concentration expected for each aqueous solution? Which would produce the highest osmotic pressure?

    a. 0.35 M KBr
    b. 0.11 M MgSO4
    c. 0.26 M $MgCl_2$
    d. 0.24 M glucose (C6H12O6)

6. The boiling point of an aqueous solution of sodium chloride is 100.37°C. What is the molality of the solution? How many grams of $NaCl$ are present in 125 g of the solution?
7. Calculate the boiling point of a solution of sugar prepared by dissolving 8.4 g of glucose ($C_6H_{12}O_6$) in 250 g of water.
8. At 37°C, the vapor pressure of 300.0 g of water was reduced from 0.062 atm to 0.058 atm by the addition of NaBr. How many grams of NaBr were added?
9. How many grams of KCl must be added to reduce the vapor pressure of 500.0 g of H_2O from 17.5 mmHg to 16.0 mmHg at 20.0°C?
10. How much $NaCl$ would you have to add to 2.0 L of water at a mountain lodge at an elevation of 7350 ft, where the pressure is 0.78 atm and the boiling point of water is 94°C, to get the water to boil at the same temperature as in New Orleans, Louisiana, where the pressure is 1.00 atm?
11. You have three solutions with the following compositions: 12.5 g of KCl in 250 mL of water, 12.5 g of glucose in 400 mL of water, and 12.5 g of $MgCl_2$ in 350 mL of water. Which will have the highest boiling point?
12. Assuming the price per kilogram is the same, which is a better salt to use for deicing wintry roads—$NaCl$ or $MgCl_2$? Why? Would magnesium chloride be an effective deicer at a temperature of −8°C?
13. How many grams of KNO_3 must be added to water to produce the same boiling point elevation as a solution of 2.03 g of $MgCl_2$ in a total volume of 120.0 mL of solution, assuming complete dissociation? If the van't Hoff factor for $MgCl_2$ at this concentration is 2.73, how much KNO_3 would be needed?
14. Calculate the quantity of each compound that would need to be added to lower the freezing point of 500.0 mL of water by 1.0°C: KBr, ethylene glycol, $MgBr_2$, ethanol. Assume that the density of water is 1.00 g/cm^3.
15. The melting point depression of biphenyl (melting point = 69.0°C) can be used to determine the molecular mass of organic compounds. A mixture of 100.0 g of biphenyl and 2.67 g of naphthalene ($C_{10}H_8$) has a melting point of 68.50°C. If a mixture of 1.00 g of an unknown compound with 100.0 g of biphenyl has a melting point of 68.86°C, what is the molar mass of the

unknown compound?

16. Four solutions of urea in water were prepared, with concentrations of 0.32 m, 0.55 m, 1.52 m, and 3.16 m. The freezing points of these solutions were found to be −0.595°C, −1.02°C, −2.72°C, and −5.71°C, respectively. Graphically determine the freezing point depression constant for water. A fifth solution made by dissolving 6.22 g of urea in 250.0 g of water has a freezing point of −0.75°C. Use these data to determine the molar mass of urea.
17. The term osmolarity has been used to describe the total solute concentration of a solution (generally water), where 1 osmole (Osm) is equal to 1 mol of an ideal, nonionizing molecule.
    a. What is the osmolarity of a 1.5 M solution of glucose? a 1.5 M solution of $NaCl$? a 1.5 M solution of $CaCl_2$?
    b. What is the relationship between osmolarity and the concentration of water?
    c. What would be the direction of flow of water through a semipermeable membrane separating a 0.1 M solution of $NaCl$ and a 0.1 M solution of $CaCl_2$?
18. At 40°C, the vapor pressures of pure CCl_4 and cyclohexane are 0.2807 atm and 0.2429 atm, respectively. Assuming ideal behavior, what is the vapor pressure of a solution with a CCl_4 mole fraction of 0.475? What is the mole fraction of cyclohexane in the vapor phase? The boiling points of CCl_4 and cyclohexane are 76.8°C and 80.7°C, respectively.
19. A benzene/toluene solution with a mole fraction of benzene of 0.6589 boils at 88°C at 1 atm. The vapor pressures of pure benzene and toluene at this temperature are 1.259 atm and 0.4993 atm, respectively. What is the composition of the vapor above the boiling solution at this temperature?
20. Plot the vapor pressure of the solution versus composition for the system $CCl_4 : CH_3CN$ at 45°C, given the following experimental data:

$X_{CCl_4}(liquid)$	0.035	0.375	0.605	0.961
$X_{CCl_4}(vapor)$	0.180	0.543	0.594	0.800
Total P (atm)	0.326	0.480	0.488	0.414

- **Source: Adapted from L. Brown and W. Foch, Australian Journal of Chemistry, 9 (1956): 180.**

- Does your diagram show behavior characteristic of an ideal solution? Explain your answer.

Numerical Answers

1. $6.7 \times 10^4\ amu$

3. 9.24 atm

5. The $CaCl_2$ solution will have a lower vapor pressure, because it contains three times as many particles as the glucose solution.

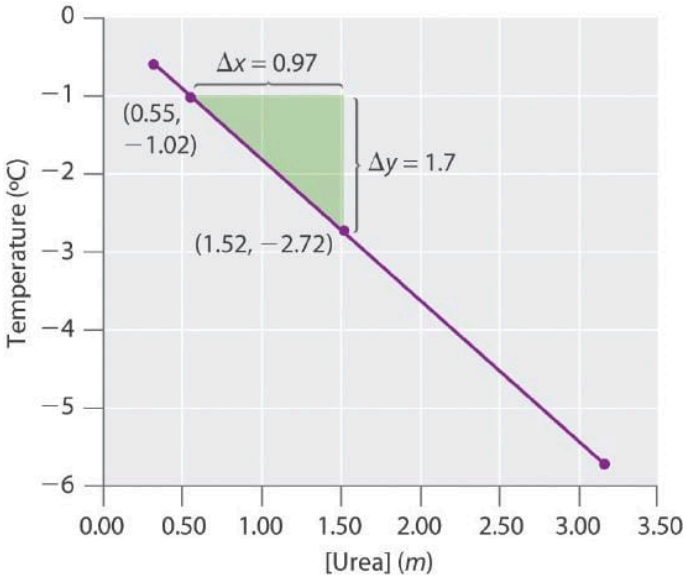
7. 0.36 m $NaCl$, 2.6 g $NaCl$

9. 60 g NaBr

11. 700 g $NaCl$

13. $MgCl_2$ produces three particles in solution versus two for $NaCl$, so the same molal concentration of $MgCl_2$ will produce a 50% greater freezing point depression than for $NaCl$. Nonetheless, the molar mass of $MgCl_2$ is 95.3 g/mol versus 48.45 g/mol for $NaCl$. Consequently, a solution containing 1 g $NaCl$ per 1000 g H_2O will produce a freezing point depression of 0.064°C versus 0.059°C for a solution containing 1 g $MgCl_2$ per 1000 g H_2O. Thus, given equal cost per gram, $NaCl$ is more effective. Yes, $MgCl_2$ would be effective at −8°C; a 1.43 m solution (136 g per 1000 g H2O) would be required.

16.



k_f = 1.81(°C•kg)/mol, molecular mass of urea = 60.0 g/mol

13.6: Colloids

Conceptual Problems

1. How does a colloid differ from a suspension? Which has a greater effect on solvent properties, such as vapor pressure?
2. Is homogenized milk a colloid or a suspension? Is human plasma a colloid or a suspension? Justify your answers.
3. How would you separate the components of an emulsion of fat dispersed in an aqueous solution of sodium chloride?

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13.S: Properties of Solutions (Summary)

These is a summary of key concepts of the chapter in the Textmap created for "Chemistry: The Central Science" by Brown et al.

13.1: The Solution Process

- **interaction between solute and solvent molecules**
- **hydration** – solvation when solvent is water

13.1.1 Energy Changes and Solution Formation

- overall enthalpy change in formation of a solution
  - $\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$
    - $\Delta H_1 =$ separation of solute molecules
    - $\Delta H_1 =$ separation of solvent molecules
    - $\Delta H_3 =$ formation of solute-solvent interactions
- separation of solute particles is endothermic
- separation of solvent is endothermic
- third is exothermic
- formation of solution can be either exothermic or endothermic
- exothermic processes are spontaneous
- solution will not form if enthalpy is too endothermic
- H_3 has to be comparable to H_1 + H_2
  - Ionic substances cannot dissolve in nonpolar liquids
  - Polar liquids do not form solutions with nonpolar liquids

13.1.2 Solution Formation, Spontaneity, and Disorder

- two nonpolar substances dissolve in one another
- attractive forces = London dispersion forces
- two factors in processes that are spontaneous: energy and disorder
- processes in which the energy content of the system decreases tend to occur spontaneously
  - exothermic
- processes in which the disorder of the system increases tend to occur spontaneously
- solutions will form unless solute-solute or solvent-solvent interactions too strong relative to solute-solvent interactions

13.1.3 Solution Formation and Chemical Reactions

- distinguish between physical process of solution formation from chemical process that leads to a solution

13.2: Saturated Solutions and Solubility

- **crystallization** – reverse process of solution
- dynamic equilibrium – when equilibrium exists between process of solution and crystallization
- solute said to be saturated
- **solubility** – amount of solute needed to saturate a solution
- **unsaturated** – when there isn't enough solute to saturate a solution
- **supersaturated** – when there is more solute than needed to saturate a solution
- for most salts crystallization of excess solute is exothermic

13.3: Factors Affecting Solubility

Solute-Solvent Interactions

- solubility increases with increasing molar mass
- London dispersion forces increase with increasing size and mass of gas molecules
- **Miscible** – pairs of liquids that mix in all proportions
- **Immiscible** – opposite of miscible
- Hydrogen-bonding interactions between solute and solvent leads to high solubility
- Substances with similar intermolecular attractive forces tend to be soluble in one another
- "like dissolves like"

Pressure Effects

- solubility of a gas in any solvent increases as pressure of gas over solvent increases
- relationship between pressure and solubility: Henry's Law:
  - $C_g = kP_g$
  - C_g solubility of gas in solution phase (usually expressed as molarity), P_g partial pressure of gas over solution, k is proportionality constant (Henry's Law constant)
  - Henry's law constant different fore each solute-solvent pair, and temperature

Temperature Effects

- solubility of most solid solutes in water increases as temperature of solution increase
- solubility of gases in water decreases with increasing temperature
- decreases solubility of O_2 in water as temperature increases in one the effects of thermal pollution

13.4: Ways of Expressing Concentration

- dilute and concentrated used to describe solution qualitatively
- mass percentage of component in solution:

$$mass = \frac{mass\ of\ component\ in\ soln}{total\ mass\ of\ soln} \times 100$$

- very dilute solutions expressed in parts per million (ppm)

$$ppm\ of\ component = \frac{mass\ of\ component\ in\ soln}{total\ mass\ of\ soln} \times 10^6$$

- 1ppm = 1g solute for each (10^6) grams of solution or 1mg solute per kg solution
- 1ppm = 1mg solute/L solution
- 1 ppb = 1g of solute/10^9 grams of solution or 1 m g solute/ L of solution

13.4.1 Mole Fraction, Molarity, and Molality

$$mole\ fraction\ of\ component = \frac{moles\ of\ component}{total\ moles\ of\ all\ components}$$

- sum of mole fractions of all components of solution must equal one
- $molarity = \frac{moles\ solute}{liters\ soln}$
- $molality = \frac{moles\ solute}{kilograms\ of\ solvent}$
- molality goes not vary with temperature
- molarity changes with temperature because of expansion and contraction of solution

13.5: Colligative Properties

Colligative properties are physical properties that depend on quantity

Lowering the Vapor Pressure

- vapor pressure over pure solvent higher than that over solution
- vapor pressure needed to obtain equilibrium of pure solvent higher than that of solution

Raoult's Law

- Raoult's law: $P_A = X_A P_A^\circ$
  - P_A = vapor pressure of solution, X_A = mole fraction of solvent, P_A° = vapor pressure of the pure solvent
  - **Ideal solution** – solution that obeys Raoult's law
  - Solute concentration is low, solute and solvent have similar molecular sizes and similar types of intermolecular attractions

Boiling-Point Elevation

- normal boiling point of pure liquid is the temperature at which pressure is 1 atm
- addition of a nonvolatile solute lowers vapor pressure of solution
- $\Delta T_b = K_b m$
- K_b = molal boiling-point-elevation constant
  - Depends only on solvent
  - boiling point elevation proportional to number of solute particles present in given quantity of solution

Freezing-Point Depression

- freezing point of solution is temperature at which the first crystals of pure solvent form in equilibrium
- freezing point of solution lower than pure liquid
- freezing point directly proportional to the molality of the solute:
  - $\Delta T_f = K_f m$
  - K_f = molal freezing-point-depression constant

Osmosis

- **semipermeable** – membranes that allow passage of some molecules and not others
- **osmosis** – the net movement of solvent molecules from the less concentrated solution to the more concentrated solution
- net movement of solvent always toward the solution with the higher solute concentration
- osmotic pressure – pressure needed to prevent osmosis, p
  - $\pi = \left(\frac{n}{V}\right) RT = MRT$
  - M = molarity of solution
- if solutions identical osmosis will not occur and said to be **isotonic**
- if one solution lower osmotic pressure = **hypotonic**, the solution that has higher osmotic pressure = **hypertonic**
- **crenation** = when cells shrivel up from the loss of water
- **hemolysis** = when cells rupture due to to much water

Determination of Molar Mass

- colligative properties can be used to find molar mass

13.6: Colloids

Colloidal dispersions (colloids) are intermediate types of dispersions or suspensions

- intermediate solutions between solutions and heterogeneous mixtures
- colloids can be gases, liquids, or solids
- colloid particles have size between 10 - 2000Å

- tyndall effect – scattering of light by colloids

Hydrophilic and Hydrophobic Colloids

- **hydrophilic** – colloids in which the dispersion medium is water
- **hydrophobic** – colloids not dispersed in water
- hydrophobic colloids have to be stabilized before being put in water
  - natural lack of affinity for water causes separation
  - can be stabilized by the adsorption of ions on the surface
  - adsorped ions interact with water
  - can also be stabilized by presence of other hydrophilic groups on surface

Removal of Colloidal Particles

- **coagulation** – enlarging colloidal particles
  - heating or adding an electrolyte to mixture
  - heating increases number of collisions and particles stick together increasing their size
  - electrolytes causes neutralization of the surface charges of the particles which remove the electrostatic repulsion
  - **dialysis** – use of semipermeable membranes to filter out colloidal particles

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14: CHEMICAL KINETICS

This chapter will present a quantitative description of when the chemical composition of a system is *not* constant with time. Chemical kinetics is the study of reaction rates, the changes in the concentrations of reactants and products with time. With a discussion of chemical kinetics, the reaction rates or the changes in the concentrations of reactants and products with time are studied. The techniques you are about to learn will enable you to describe the speed of many such changes and predict how the composition of each system will change in response to changing conditions. As you learn about the factors that affect reaction rates, the methods chemists use for reporting and calculating those rates, and the clues that reaction rates provide about events at the molecular level.

14.1: Factors that Affect Reaction Rates

14.2: Reaction Rates

14.3: Concentration and Rates (Differential Rate Laws)

14.4: The Change of Concentration with Time (Integrated Rate Laws)

14.5: Temperature and Rate

14.6: Reaction Mechanisms

14.7: Catalysis

14.E: Exercises

14.S: Chemical Kinetics (Summary)

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14.1: Factors that Affect Reaction Rates

Learning Objectives

- To gain a general overview of some of the important factors that manipulate chemical reaction rates.

There are many factors that influence the reaction rates of chemical reactions include the concentration of reactants, temperature, the physical state of reactants and their dispersion, the solvent, and the presence of a catalyst.

Although a balanced chemical equation for a reaction describes the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed, it gives us no information about whether or how fast a given reaction will occur. This information is obtained by studying the chemical kinetics of a reaction, which depend on various factors: reactant concentrations, temperature, physical states and surface areas of reactants, and solvent and catalyst properties if either are present. By studying the kinetics of a reaction, chemists gain insights into how to control reaction conditions to achieve a desired outcome.

Concentration Effects

Two substances cannot possibly react with each other unless their constituent particles (molecules, atoms, or ions) come into contact. If there is no contact, the reaction rate will be zero. Conversely, the more reactant particles that collide per unit time, the more often a reaction between them can occur. Consequently, the reaction rate usually increases as the concentration of the reactants increases.

Temperature Effects

Increasing the temperature of a system increases the average kinetic energy of its constituent particles. As the average kinetic energy increases, the particles move faster and collide more frequently per unit time and possess greater energy when they collide. Both of these factors increase the reaction rate. Hence the reaction rate of virtually all reactions increases with increasing temperature. Conversely, the reaction rate of virtually all reactions decreases with decreasing temperature. For example, refrigeration retards the rate of growth of bacteria in foods by decreasing the reaction rates of biochemical reactions that enable bacteria to reproduce.

In systems where more than one reaction is possible, the same reactants can produce different products under different reaction conditions. For example, in the presence of dilute sulfuric acid and at temperatures around 100°C, ethanol is converted to diethyl ether:

$$2\mathrm{CH_3CH_2OH} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{CH_3CH_2OCH_2CH_3} + \mathrm{H_2O} \tag{14.1.1}$$

At 180°C, however, a completely different reaction occurs, which produces ethylene as the major product:

$$\mathrm{CH_3CH_2OH} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{C_2H_4} + \mathrm{H_2O} \tag{14.1.2}$$

Phase and Surface Area Effects

When two reactants are in the same fluid phase, their particles collide more frequently than when one or both reactants are solids (or when they are in different fluids that do not mix). If the reactants are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time depends on concentration and temperature, as we have just seen. If the reaction is heterogeneous, however, the reactants are in two different phases, and collisions between the reactants can occur only at interfaces between phases. The number of collisions between reactants per unit time is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase.

Automobile engines use surface area effects to increase reaction rates. Gasoline is injected into each cylinder, where it combusts on ignition by a spark from the spark plug. The gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided flour burns slowly (or not at all), but spraying finely divided flour into a flame produces a vigorous reaction.

Solvent Effects

The nature of the solvent can also affect the reaction rates of solute particles. For example, a sodium acetate solution reacts with methyl iodide in an exchange reaction to give methyl acetate and sodium iodide.

$$CH_3CO_2Na_{(soln)} + CH_3I_{(l)} \rightarrow CH_3CO_2CH_{3\ (soln)} + NaI_{(soln)} \tag{14.1.3}$$

This reaction occurs 10 million times more rapidly in the organic solvent dimethylformamide [DMF; $(CH_3)_2NCHO$] than it does in methanol (CH_3OH). Although both are organic solvents with similar dielectric constants (36.7 for DMF versus 32.6 for methanol), methanol is able to hydrogen bond with acetate ions, whereas DMF cannot. Hydrogen bonding reduces the reactivity of the oxygen atoms in the acetate ion.

Solvent viscosity is also important in determining reaction rates. In highly viscous solvents, dissolved particles diffuse much more slowly than in less viscous solvents and can collide less frequently per unit time. Thus the reaction rates of most reactions decrease rapidly with increasing solvent viscosity.

Catalyst Effects

A catalyst is a substance that participates in a chemical reaction and increases the reaction rate without undergoing a net chemical change itself. Consider, for example, the decomposition of hydrogen peroxide in the presence and absence of different catalysts. Because most catalysts are highly selective, they often determine the product of a reaction by accelerating only one of several possible reactions that could occur.

Most of the bulk chemicals produced in industry are formed with catalyzed reactions. Recent estimates indicate that about 30% of the gross national product of the United States and other industrialized nations relies either directly or indirectly on the use of catalysts.

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14.2: Reaction Rates

Learning Objectives

- To determine the reaction rate of a reaction.

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

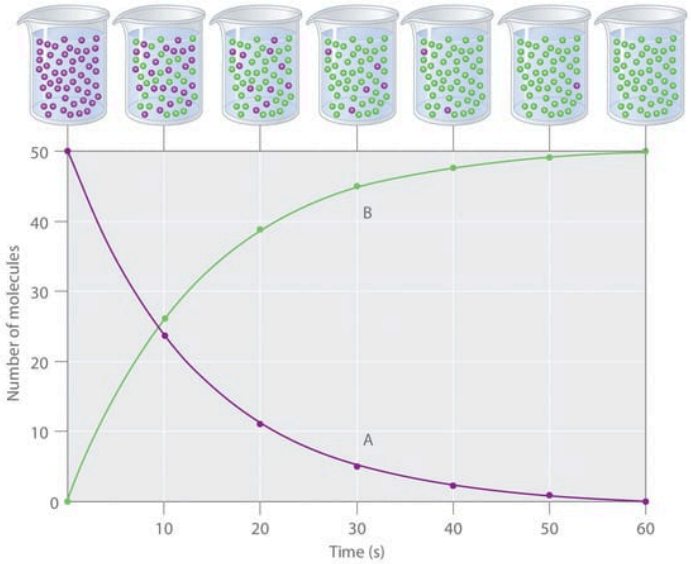


Figure 14.2.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure 14.2.1; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 14.2.1. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{14.2.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 14.2.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

Reaction rates generally decrease with time as reactant concentrations decrease.

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A Video Discussing Average Reaction Rates. Video Link: Introduction to Chemical Reaction Kinetics(opens in new window) [youtu.be] (opens in new window)

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 14.2.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure 14.2.2.

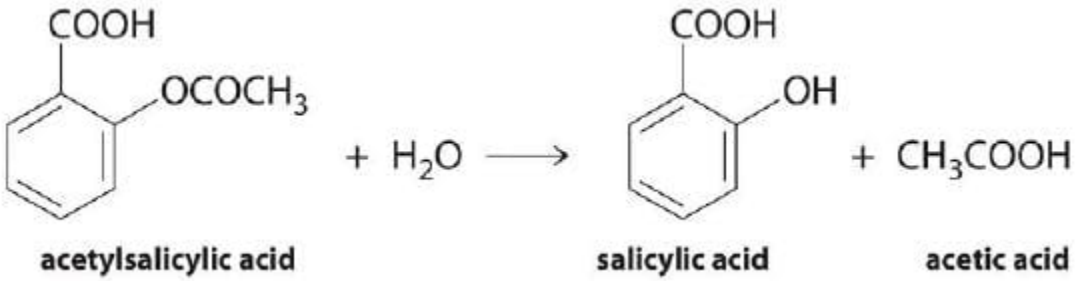


Figure 14.2.2: Hydrolysis of Aspirin reaction.

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 14.2.1 and are shown in the graph in Figure 14.2.3.

*Table 14.2.1: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C**

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}

***The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.**

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
300	1.82×10^{-3}	3.73×10^{-3}
***The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.**		

The data in Table 14.2.1 were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

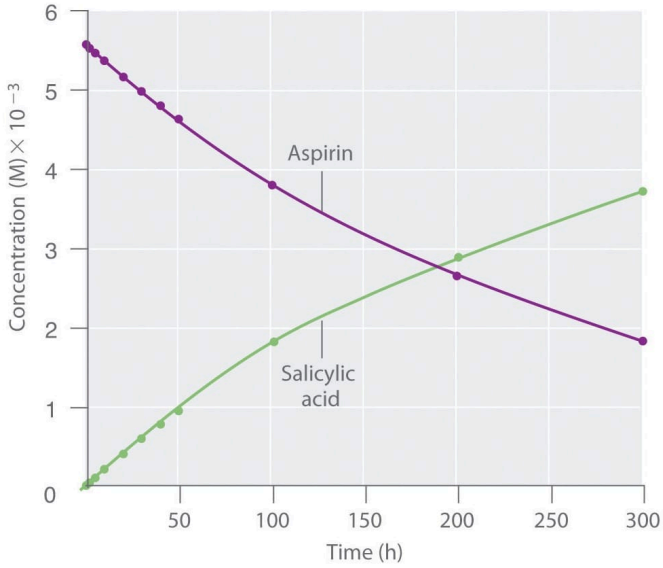


Figure 14.2.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

Graph of concentration against time in hours. The purple line is aspirin. The green line is salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= \frac{0.040 \times 10^{-3}\text{ M} - 0\text{ M}}{2.0\text{ h}} = 2.0 \times 10^{-5}\text{ M/h}\end{aligned}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= -\frac{(5.51 \times 10^{-3}\text{ M}) - (5.55 \times 10^{-3}\text{ M})}{2.0\text{ h}} \\ &= 2 \times 10^{-5}\text{ M/h}\end{aligned}$$

If the reaction rate is calculated during the last interval given in Table 14.2.1(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\begin{aligned}\text{rate}_{(t=200-300\text{h})} &= \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\text{ h} - 200\text{ h}} \\ &= -\frac{(3.73 \times 10^{-3}\text{ M}) - (2.91 \times 10^{-3}\text{ M})}{100\text{ h}} \\ &= 8.2 \times 10^{-6}\text{ M/h}\end{aligned}$$

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{\mathrm{C_{12}H_{22}O_{11}(aq)}} + \mathrm{H_2O(l)} \rightarrow 4\mathrm{C_2H_5OH(aq)} + 4\mathrm{CO_2(g)} \tag{14.2.2}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10, the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[\mathrm{C_2H_5OH}]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{14.2.3}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 14.2.3 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 14.2.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[\mathrm{C_2H_5OH}]}{\Delta t}\right) \tag{14.2.4}$$

Example 14.2.1: Decomposition Reaction I

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2\mathrm{N_2O_5(g)} \xrightarrow{\Delta} 4\mathrm{NO_2(g)} + \mathrm{O_2(g)}$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.
B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t}$$

Exercise 14.2.1: Contact Process I

The contact process is used in the manufacture of sulfuric acid. A key step in this process is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer available at the end of this section.

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, t = 0. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to t = 0.

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Example 14.2.2: Decomposition Reaction II

Using the reaction shown in Example 14.2.1, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

calculate the reaction rate from the following data taken at 56°C:

Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example 14.2.1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.
B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example 14.2.1, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t} = -\frac{[\text{N}_2\text{O}_5]_{600} - [\text{N}_2\text{O}_5]_{240}}{2(600\ \text{s} - 240\ \text{s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197\ \text{M} - 0.0388\ \text{M}}{2(360\ \text{s})} = 2.65 \times 10^{-5}\ \text{M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = \frac{[\text{NO}_2]_{600} - [\text{NO}_2]_{240}}{4(600\ \text{s} - 240\ \text{s})} = \frac{0.0699\ \text{M} - 0.0314\ \text{M}}{4(360\ \text{s})} = 2.67 \times 10^{-5}\ \text{M/s}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{[\text{O}_2]_{600} - [\text{O}_2]_{240}}{600\ \text{s} - 240\ \text{s}} = \frac{0.0175\ \text{M} - 0.00792\ \text{M}}{360\ \text{s}} = 2.66 \times 10^{-5}\ \text{M/s}$$

Again, this is the same value obtained from the N_2O_5 and NO_2 data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

Exercise 14.2.2: Contact Process II

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

Time (s)	[SO_2] (M)	[O_2] (M)	[SO_3] (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer: available at the end of this section.

Summary

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. Reaction rates can be determined over particular time intervals or at a given point in time.

- General definition of rate for A → B:

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t}$$

Answers

Exercise 14.2.1**: Contact Process I**

$$\text{rate} = -\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{\Delta[\text{SO}_2]}{2\Delta t} = \frac{\Delta[\text{SO}_3]}{2\Delta t}$$

Exercise 14.2.2**: Contact Process II**

9.0×10^{-6} M/s

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14.3: Concentration and Rates (Differential Rate Laws)

Learning Objectives

- To understand the meaning of the rate law.

The factors that affect the reaction rate of a chemical reaction, which may determine whether a desired product is formed. In this section, we will show you how to quantitatively determine the reaction rate.

Rate Laws

Typically, reaction rates decrease with time because reactant concentrations decrease as reactants are converted to products. Reaction rates generally increase when reactant concentrations are increased. This section examines mathematical expressions called **rate laws**, which describe the relationships between reactant rates and reactant concentrations. Rate laws are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A **differential rate law** expresses the reaction rate in terms of changes in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δt). In contrast, an **integrated rate law** describes the reaction rate in terms of the initial concentration ($[R]_0$) and the measured concentration of one or more reactants ([R]) after a given amount of time (t); integrated rate laws are discussed in more detail later. The integrated rate law is derived by using calculus to integrate the differential rate law. Whether using a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).

Reaction Orders

For a reaction with the general equation:

$$aA + bB \rightarrow cC + dD \tag{14.3.1}$$

the experimentally determined rate law usually has the following form:

$$\text{rate} = k[A]^m[B]^n \tag{14.3.2}$$

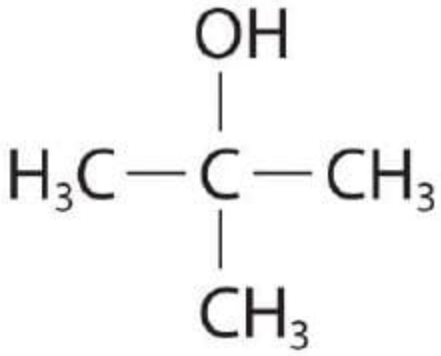
The proportionality constant (*k*) is called the **rate constant**, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular rate constant value under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of *k*, however, does not change as the reaction progresses under a given set of conditions.

> Under a given set of conditions, the value of the rate constant does **not** change as the reaction progresses.

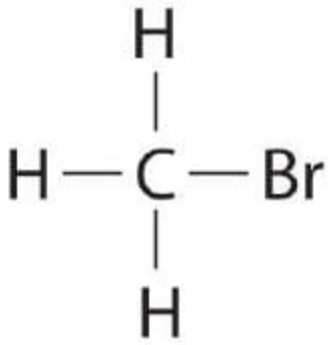
The reaction rate thus depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers *m* and *n*, respectively. The values of *m* and *n* are derived from experimental measurements of the changes in reactant concentrations over time and indicate the **reaction order**, the degree to which the reaction rate depends on the concentration of each reactant; *m* and *n* need not be integers. For example, Equation 14.3.2 tells us that Equation 14.3.1 is m^{th} order in reactant A and n^{th} order in reactant B. It is important to remember that *n* and *m* are not related to the stoichiometric coefficients *a* and *b* in the balanced chemical equation and must be determined **experimentally**. The overall reaction order is the sum of all the exponents in the rate law: *m* + *n*.

> *The orders of the reactions (e.g. n and m)* are **not** related to the stoichiometric coefficients in the balanced chemical (e.g., *a* and *b*).

To illustrate how chemists interpret a differential rate law, consider the experimentally derived rate law for the hydrolysis of *t*-butyl bromide in 70% aqueous acetone.



t-butanol



methyl bromide

This reaction produces *t*-butanol according to the following equation:

$$(CH_3)_3CBr_{(soln)} + H_2O_{(soln)} \rightarrow (CH_3)_3COH_{(soln)} + HBr_{(soln)} \tag{14.3.3}$$

Combining the rate expression in Equation 14.3.2 with the definition of average reaction rate

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t}$$

gives a general expression for the differential rate law:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^m[\text{B}]^n \tag{14.3.4}$$

Inserting the identities of the reactants into Equation 14.3.4 gives the following expression for the differential rate law for the reaction:

$$\text{rate} = -\frac{\Delta[(\text{CH}_3)_3\text{CBr}]}{\Delta t} = k[(\text{CH}_3)_3\text{CBr}]^m[\text{H}_2\text{O}]^n \tag{14.3.5}$$

Experiments to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(CH_3)_3CBr$ but is independent of the concentration of water. Therefore, m and n in Equation 14.3.4 are 1 and 0, respectively, and,

$$\text{rate} = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr] \tag{14.3.6}$$

Because the exponent for the reactant is 1, the reaction is first order in $(CH_3)_3CBr$. It is zeroth order in water because the exponent for $[H_2O]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus, the overall reaction order is 1 + 0 = 1. The reaction orders state in practical terms that doubling the concentration of $(CH_3)_3CBr$ doubles the reaction rate of the hydrolysis reaction, halving the concentration of $(CH_3)_3CBr$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has no effect on the reaction rate. (Again, when working with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of *k*, *m*, and *n* in the rate law must be determined experimentally.) Experimental data show that *k* has the value 5.15×10^{-4} s^{-1} at 25°C. The rate constant has units of reciprocal seconds (s^{-1}) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH_3Br) is as follows:

$$\text{rate} = -\frac{\Delta[\text{CH}_3\text{Br}]}{\Delta t} = k'[\text{CH}_3\text{Br}] \tag{14.3.7}$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 14.3.7 is approximately 10^6 times smaller

than that for *t*-butyl bromide. Thus, methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often alter reaction conditions to study the mechanics of a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH^- ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. In contrast, for methyl bromide, the differential rate law becomes

$$\text{rate} = k''[CH_3Br][OH^-]$$

with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, providing clues as to how the reactions differ on a molecular level.

Example 14.3.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g)$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[{\text{NO}_2}^m][\text{CO}]^n$$

The reaction is second order in NO_2; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k[{\text{NO}_2}^2][\text{CO}]^0 = k[{\text{NO}_2}^2]$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Exercise 14.3.1A

The rate law for the reaction:

$$\text{H}_2(g) + 2\,\text{NO}(g) \longrightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g)$$

has been experimentally determined to be $rate = k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2
- order in H_2 = 1
- overall order = 3

Exercise 14.3.1B

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$CH_3OH + CH_3CH_2OCOCH_3 \longrightarrow CH_3OCOCH_3 + CH_3CH_2OH$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[CH_3OH]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1
- order in $CH_3CH_2OCOCH_3$ = 0
- overall order = 1

Example 14.3.2: Differential Rate Laws

Below are three reactions and their experimentally determined differential rate laws. For each reaction, give the units of the rate constant, give the reaction order with respect to each reactant, give the overall reaction order, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.

a.
$$2HI(g) \xrightarrow{Pt} H_2(g) + I_2(g)$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[HI]}{\Delta t}\right) = k[HI]^2$$

b.
$$2N_2O(g) \xrightarrow{\Delta} 2N_2(g) + O_2(g)$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = k$$

c.
$$\text{cyclopropane(g)} \rightarrow \text{propane(g)}$$
$$\text{rate} = -\frac{\Delta[\text{cyclopropane}]}{\Delta t} = k[\text{cyclopropane}]$$

Given: balanced chemical equations and differential rate laws

Asked for: units of rate constant, reaction orders, and effect of doubling reactant concentration

Strategy:

A. Express the reaction rate as moles per liter per second [mol/(L·s), or M/s]. Then determine the units of each chemical species in the rate law. Divide the units for the reaction rate by the units for all species in the rate law to obtain the units for the rate constant.
B. Identify the exponent of each species in the rate law to determine the reaction order with respect to that species. Add all exponents to obtain the overall reaction order.
C. Use the mathematical relationships as expressed in the rate law to determine the effect of doubling the concentration of a single species on the reaction rate.

Solution

1. **A** $[HI]^2$ will give units of (moles per liter)^2. For the reaction rate to have units of moles per liter per second, the rate constant must have reciprocal units [1/(M·s)]:

$$k\text{M}^2 = \frac{\text{M}}{\text{s}}k = \frac{\text{M/s}}{\text{M}^2} = \frac{1}{\text{M}\cdot\text{s}} = \text{M}^{-1}\cdot\text{s}^{-1}$$

B The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second order overall.

C If the concentration of HI is doubled, the reaction rate will increase from $k[HI]_0^2$ to $k(2[HI])_0^2 = 4k[HI]_0^2$. The reaction rate will therefore quadruple.

2. **A** Because no concentration term appears in the rate law, the rate constant must have M/s units for the reaction rate to have M/s units.

   B The rate law tells us that the reaction rate is constant and independent of the N_2O concentration. That is, the reaction is zeroth order in N_2O and zeroth order overall.

   C Because the reaction rate is independent of the N_2O concentration, doubling the concentration will have no effect on the reaction rate.

3. **A** The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds (s^{-1}) to have units of moles per liter per second for the reaction rate: $M \cdot s^{-1} = M/s$.

   B The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

   C Doubling the initial cyclopropane concentration will increase the reaction rate from $k[\text{cyclopropane}]_0$ to $2k[\text{cyclopropane}]_0$. This doubles the reaction rate.

Exercise 14.3.2

Given the following two reactions and their experimentally determined differential rate laws: determine the units of the rate constant if time is in seconds, determine the reaction order with respect to each reactant, give the overall reaction order, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

a. $$\mathrm{CH_3N{=}NCH_3(g) \rightarrow C_2H_6(g) + N_2(g)} \quad \text{rate} = -\frac{\Delta[\mathrm{CH_3N{=}NCH_3}]}{\Delta t} \tag{14.3.8}$$
$$= k[\mathrm{CH_3N{=}NCH_3}] \tag{14.3.9}$$

b. $$\mathrm{2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)} \quad \text{rate} = -\frac{\Delta[\mathrm{F_2}]}{\Delta t} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{NO_2}]}{\Delta t}\right) \tag{14.3.10}$$
$$= k[\mathrm{NO_2}][\mathrm{F_2}] \tag{14.3.11}$$

Answer a available at the end of this section.

Determining the Rate Law of a Reaction

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding **reaction mechanisms** can simplify what might seem to be a confusing variety of chemical reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law. This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow products$, for example, we need to determine k and the exponents m and n in the following equation:

$$\text{rate} = k[A]^m[B]^n \tag{14.3.12}$$

To do this, we might keep the initial concentration of B constant while varying the initial concentration of A and calculating the initial reaction rate. This information would permit us to deduce the reaction order with respect to A. Similarly, we could determine the reaction order with respect to B by studying the initial reaction rate when the initial concentration of A is kept constant while the initial concentration of B is varied. In earlier examples, we determined the reaction order with respect to a given reactant by comparing the different rates obtained when only the concentration of the reactant in question was changed. An alternative way of determining reaction orders is to set up a proportion using the rate laws for two different experiments. Rate data for a hypothetical reaction of the type $A + B \rightarrow products$ are given in Table 14.3.1.

Table 14.3.1*: Rate Data for a Hypothetical Reaction of the Form* $A + B \rightarrow products$

Experiment	[A] (M)	[B] (M)	Initial Rate (M/min)
1	0.50	0.50	8.5×10^{-3}
2	0.75	0.50	19×10^{-3}
3	1.00	0.50	34×10^{-3}
4	0.50	0.75	8.5×10^{-3}
5	0.50	1.00	8.5×10^{-3}

The general rate law for the reaction is given in Equation 14.3.12. We can obtain *m* or *n* directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in Table 14.3.3.

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_3]^m[\text{B}_3]^n}$$

Inserting the appropriate values from Table 14.3.3,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{34 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[1.00\ \text{M}]^m[0.50\ \text{M}]^n}$$

Because 1.00 to any power is 1, $[1.00\ \text{M}]^m = 1.00\ \text{M}$. We can cancel like terms to give $0.25 = [0.50]^m$, which can also be written as $1/4 = [1/2]^m$. Thus we can conclude that $m = 2$ and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for *m*.

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for *n*.

$$\frac{\text{rate}_1}{\text{rate}_5} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_5]^m[\text{B}_5]^n}$$

Substituting the appropriate values from Table 14.3.3,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{8.5 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[0.50\ \text{M}]^m[1.00\ \text{M}]^n}$$

Canceling leaves $1.0 = [0.50]^n$, which gives $n = 0$; that is, the reaction is zeroth order in B. The experimentally determined rate law is therefore

$$\text{rate} = k[\text{A}]^2[\text{B}]^0 = k[\text{A}]^2$$

We can now calculate the rate constant by inserting the data from any row of Table 14.3.3 into the experimentally determined rate law and solving for k. Using Experiment 2, we obtain

$$19 \times 10^{-3}\ \text{M/min} = k(0.75\ \text{M})^2$$

$$3.4 \times 10^{-2}\ \text{M}^{-1}\cdot\text{min}^{-1} = \text{k}$$

You should verify that using data from any other row of Table 14.3.1 gives the same rate constant. This must be true as long as the

experimental conditions, such as temperature and solvent, are the same.

Example 14.3.3

Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with O_2 to give NO_2, which then reacts rapidly with water to give nitrous acid and nitric acid:

$$2NO + O_2 \longrightarrow 2NO_2 \xrightarrow{H_2O} HNO_2 + HNO_3$$

These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with O_2 at 25°C:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Determine the rate law for the reaction and calculate the rate constant.

rate law for the reaction and calculate the rate constant.

Experiment	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial Rate (M/s)
1	0.0235	0.0125	7.98×10^{-3}
2	0.0235	0.0250	15.9×10^{-3}
3	0.0470	0.0125	32.0×10^{-3}
4	0.0470	0.0250	63.5×10^{-3}

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: rate law and rate constant

Strategy:

A. Compare the changes in initial concentrations with the corresponding changes in rates of reaction to determine the reaction order for each species. Write the rate law for the reaction.
B. Using data from any experiment, substitute appropriate values into the rate law. Solve the rate equation for *k*.

Solution

A Comparing Experiments 1 and 2 shows that as $[O_2]$ is doubled at a constant value of $[NO_2]$, the reaction rate approximately doubles. Thus the reaction rate is proportional to $[O_2]^1$, so the reaction is first order in O_2. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and $[O_2]$ is held constant. That is, the reaction rate is proportional to $[NO]^2$, which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

$$\text{rate} = k[NO]^2[O_2]$$

B The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{7.98 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0125\ \text{M})} = 1.16 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1}$$

Alternatively, using Experiment 2 gives

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]} = \frac{15.9 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0250\ \text{M})} = 1.15 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1}$$

The difference is minor and associated with significant digits and likely experimental error in making the table.

The overall reaction order $(m + n) = 3$, so this is a third-order reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

Exercise 14.3.3

The peroxydisulfate ion ($S_2O_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O^{2-}_{8(aq)} + 3I^-_{(aq)} \rightarrow 2SO^{2-}_{4(aq)} + I^-_{3(aq)}$$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

kinetics data for this reaction at 25°C.

Experiment	$[S_2O_8^{2-}]_0$ (M)	$[I^-]_0$ (M)	Initial Rate (M/s)
1	0.27	0.38	2.05
2	0.40	0.38	3.06
3	0.40	0.22	1.76

Answer: available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

A Video Discussing Initial Rates and Rate Law Expressions. Video Link: Initial Rates and Rate Law Expressions(opens in new window) [youtu.be]

Summary

The rate law for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a differential rate law, describing the change in reactant or product concentrations as a function of time, or as an integrated rate law, describing the actual concentrations of reactants or products as a function of time. The rate constant (*k*) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The exponent to which a concentration is raised in a rate law indicates the reaction order, the degree to which the reaction rate depends on the concentration of a particular reactant.

Answers

Exercise 14.3.2

s^{-1}; first order in $CH_3N{=}NCH_3$; first order overall; doubling $[CH_3N{=}NCH_3]$ will double the reaction rate.

$M^{-1}{\cdot}s^{-1}$; first order in NO_2, first order in F_2; second order overall; doubling $[NO_2]$ will double the reaction rate.

Exercise 14.3.3

rate = $k[S_2O_8^{2-}][I^-]$; $k = 20\ M^{-1}\cdot s^{-1}$

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14.4: The Change of Concentration with Time (Integrated Rate Laws)

Learning Objectives

- To apply rate laws to zeroth, first and second order reactions.

Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data. Often, the exponents in the rate law are the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data. The learning objective of this Module is to know how to determine the reaction order from experimental data.

Zeroth-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is

$$\text{rate} = k.$$

We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \tag{14.4.1}$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k, a positive value.

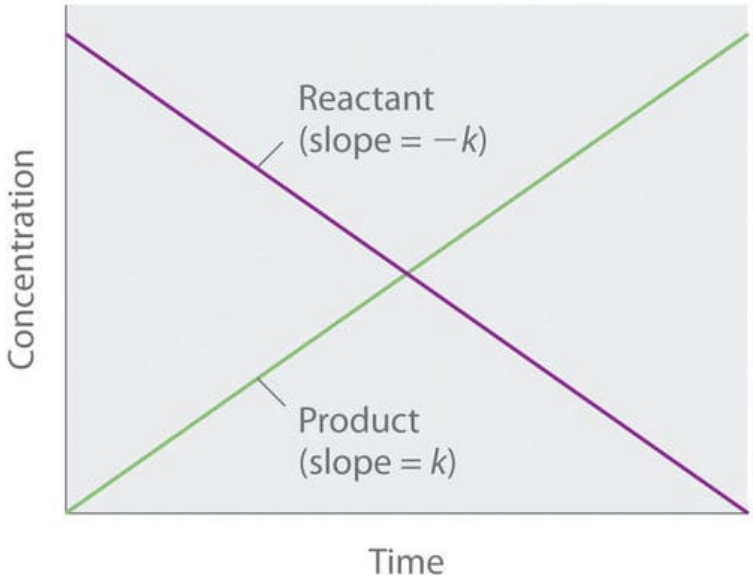


Figure 14.4.1: The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

Graph of concentration against time. The reactant is in purple and has a slope of minus k. The product is in green and has a slope of positive k.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \tag{14.4.2}$$

where $[A]_0$ is the initial concentration of reactant A. Equation 14.4.2 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = [A]$, $mx = -kt$, and $b = [A]_0$.)

Units

In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g) \tag{14.4.3}$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[N_2]}{\Delta t}\right) = \frac{\Delta[O_2]}{\Delta t} = k[N_2O]^0 = k \tag{14.4.4}$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure 14.4.2, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.

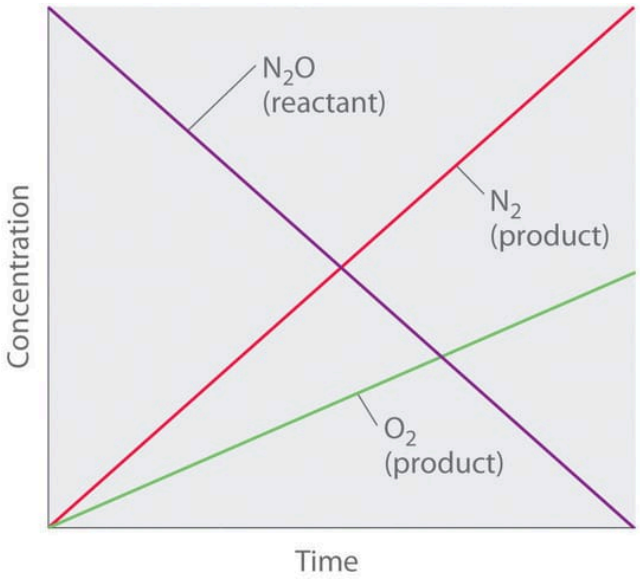


Figure 14.4.2: A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

Graph of concentration against time. N2O is the reactiant is graphed in purple. O2 is one of the products and is graphed in green. The second product is N2 which is graphed in red

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is

$$CH_3CH_2OH + NAD^+ \xrightarrow[\text{dehydrogenase}]{\text{alcohol}} CH_3\overset{\overset{O}{\|}}{C}H + NADH + H^+$$

Figure 14.4.2

where \ce{NAD^{+}}\) (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (Figure $14.4.3a$). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure $14.4.3$).

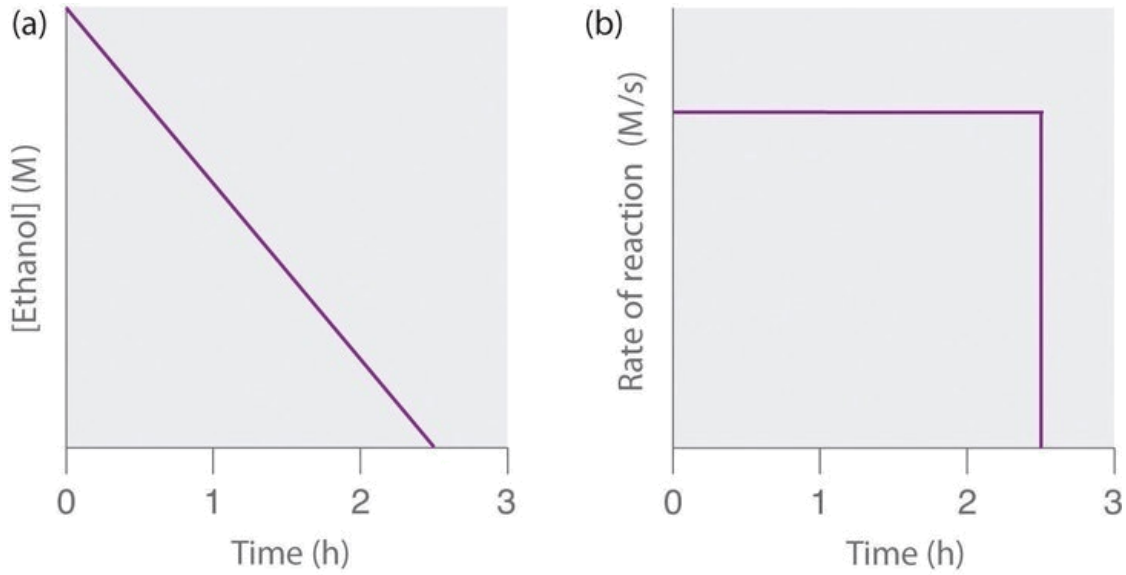


Figure 14.4.3: The Catalyzed Oxidation of Ethanol (a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

1. In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.
2. A linear change in concentration with time is a clear indication of a zeroth-order reaction.

First-Order Reactions

In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \tag{14.4.5}$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \tag{14.4.6}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 14.4.6 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 14.4.6 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[A] = \ln [A]_0 - kt \tag{14.4.7}$$

Because Equation 14.4.7 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = \ln[A]$ and $b = \ln [A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln [A]_0$. Either the differential rate law (Equation 14.4.5) or the integrated rate law (Equation 14.4.7) can be used to

determine whether a particular reaction is first order.

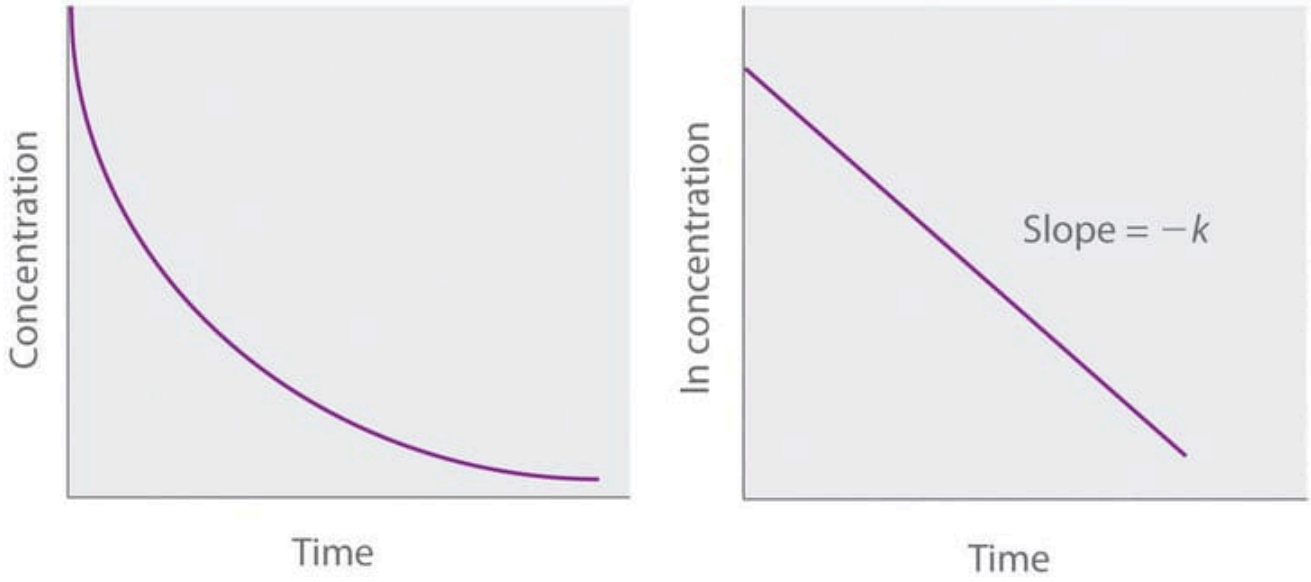


Figure 14.4.4: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. One reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin. Cisplatin, the first "inorganic" anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

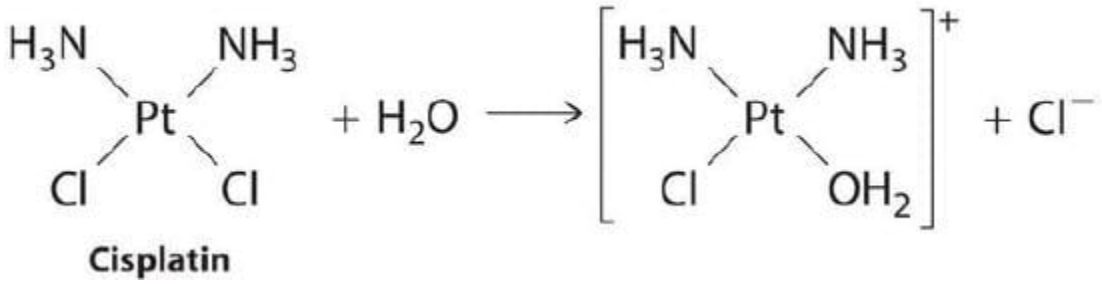


Figure 14.4.5: Cis-platin reaction with water.

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 14.4.5 is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 14.4.4 have been studied extensively to find ways of maximizing the concentration of the active species.

> If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 14.4.1. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin.

Table 14.4.1: Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	$[\text{Cisplatin}]_0$ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}

Experiment	[Cisplatin]$_0$ (M)	Initial Rate (M/min)
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table 14.4.1 shows that the reaction rate doubles [(1.8×10^{-5} M/min) ÷ (9.0×10^{-6} M/min) = 2.0] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [(4.5×10^{-5} M/min) ÷ (9.0×10^{-6} M/min) = 5.0] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate = k[cisplatin]^1. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table 14.4.1. For example, substituting the values for Experiment 3 into Equation 14.4.5,

$$3.6 \times 10^{-5} \text{ M/min} = k(0.024 \text{ M})$$

$$1.5 \times 10^{-3} \text{ min}^{-1} = k$$

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

Example 14.4.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$\mathrm{CH_3CH_2Cl\,(g)} \xrightarrow{\Delta} \mathrm{HCl\,(g) + C_2H_4\,(g)}$$

Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

data for the reaction at 650°C

Experiment	[CH_3CH_2Cl]$_0$ (M)	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

A. Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.
B. Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[CH_3CH_2Cl]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[CH_3CH_2Cl]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is rate = $k[CH_3CH_2Cl]$.

C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8} \text{ M/s} = k(0.010 \text{ M})$$

$$1.6 \times 10^{-6} \text{ s}^{-1} = k$$

Exercise 14.4.1

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Data for the reaction at 320°C

Experiment	$[SO_2Cl_2]_0$ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer available at the end of this section.

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Figure $14.4.6a$ shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

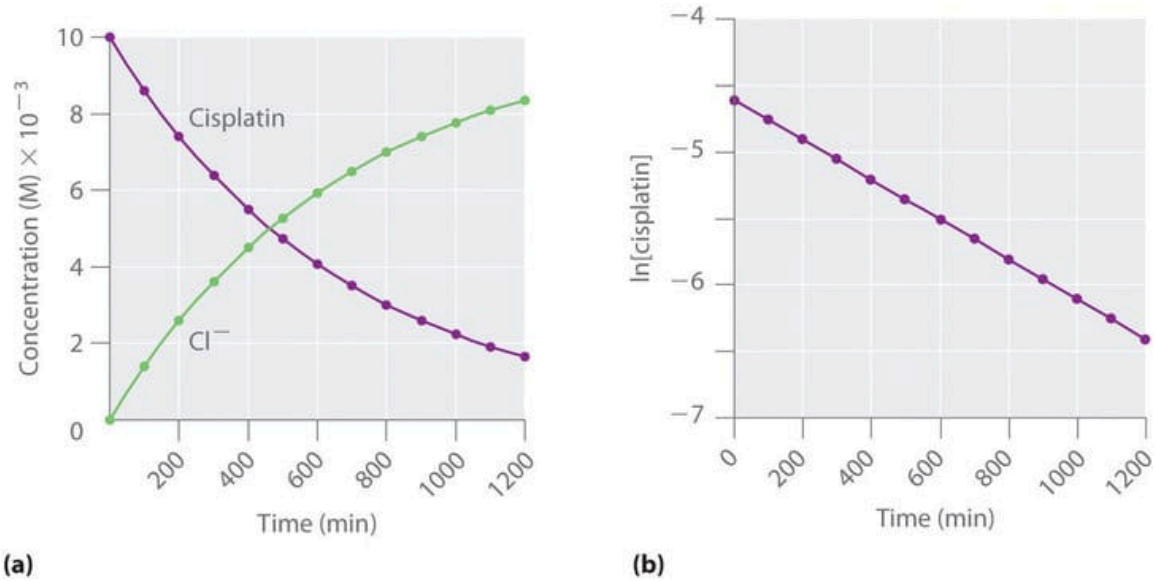


Figure 14.4.6: The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure 14.4.6. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure 14.4.6 for t = 100 min ([cisplatin] = 0.0086 M) and t = 1000 min ([cisplatin] = 0.0022 M),

$$\text{slope} = \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000\ \text{min} - 100\ \text{min}}$$

$$-k = \frac{\ln 0.0022 - \ln 0.0086}{1000\ \text{min} - 100\ \text{min}} = \frac{-6.12 - (-4.76)}{900\ \text{min}} = -1.51 \times 10^{-3}\ \text{min}^{-1}$$

$$k = 1.5 \times 10^{-3}\ \text{min}^{-1}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure 14.4.6 are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.

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Video Example Using the First-Order Integrated Rate Law Equation:

Example Using the First-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Example 14.4.2

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M (k = 1.6 × 10^{-6} s^{-1}) ?

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:

A. Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ([A]) at the given time t.
B. Given a concentration [A], solve the integrated rate law for time t.

Solution

The exponential form of the integrated rate law for a first-order reaction (Equation 14.4.6) is $[A] = [A]_0 e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of k = 1.6 × 10^{-6} s^{-1}, we can use the rate law to calculate the concentration of the reactant at a given time t. Substituting the known values into the integrated rate law,

$$\begin{aligned}[\mathrm{CH_3CH_2Cl}]_{10\ \mathrm{h}} &= [\mathrm{CH_3CH_2Cl}]_0 e^{-kt} \\ &= 0.0200\ \mathrm{M}(e^{-(1.6\times10^{-6}\ \mathrm{s^{-1}})[(10\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min})]}) \\ &= 0.0189\ \mathrm{M}\end{aligned}$$

We could also have used the logarithmic form of the integrated rate law (Equation 14.4.7):

$$\begin{aligned}\ln[\mathrm{CH_3CH_2Cl}]_{10\ \mathrm{h}} &= \ln[\mathrm{CH_3CH_2Cl}]_0 - kt \\ &= \ln 0.0200 - (1.6\times10^{-6}\ \mathrm{s^{-1}})[(10\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min})] \\ &= -3.912 - 0.0576 = -3.970 \\ [\mathrm{CH_3CH_2Cl}]_{10\ \mathrm{h}} &= e^{-3.970}\ \mathrm{M} \\ &= 0.0189\ \mathrm{M}\end{aligned}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 14.4.7 gives the following:

$$\ln [CH_3CH_2Cl]_t = \ln [CH_3CH_2Cl]_0 - kt$$

$$kt = \ln [CH_3CH_2Cl]_0 - \ln [CH_3CH_2Cl]_t = \ln \frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}$$

$$t = \frac{1}{k}\left(\ln \frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}\right) = \frac{1}{1.6 \times 10^{-6}\ \text{s}^{-1}}\left(\ln \frac{0.0200\ \text{M}}{0.0050\ \text{M}}\right)$$

$$= \frac{\ln 4.0}{1.6 \times 10^{-6}\ \text{s}^{-1}} = 8.7 \times 10^5\ \text{s} = 240\ \text{h} = 2.4 \times 10^2\ \text{h}$$

Exercise 14.4.2

In the exercise in Example 14.4.1, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C.

a. Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C.
b. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer a available at the end of this section.

Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form

$$2\,A \longrightarrow \text{products}\cdot$$

A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$\text{rate} = -\frac{\Delta[A]}{2\Delta t} = k[A]^2 \tag{14.4.8}$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1}{\cdot}s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \tag{14.4.9}$$

Because Equation 14.4.9 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of 1/[A] versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.

Second-order reactions generally have the form 2A → products or A + B → products.

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Video Discussing the Second-Order Integrated Rate Law Equation: Second-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

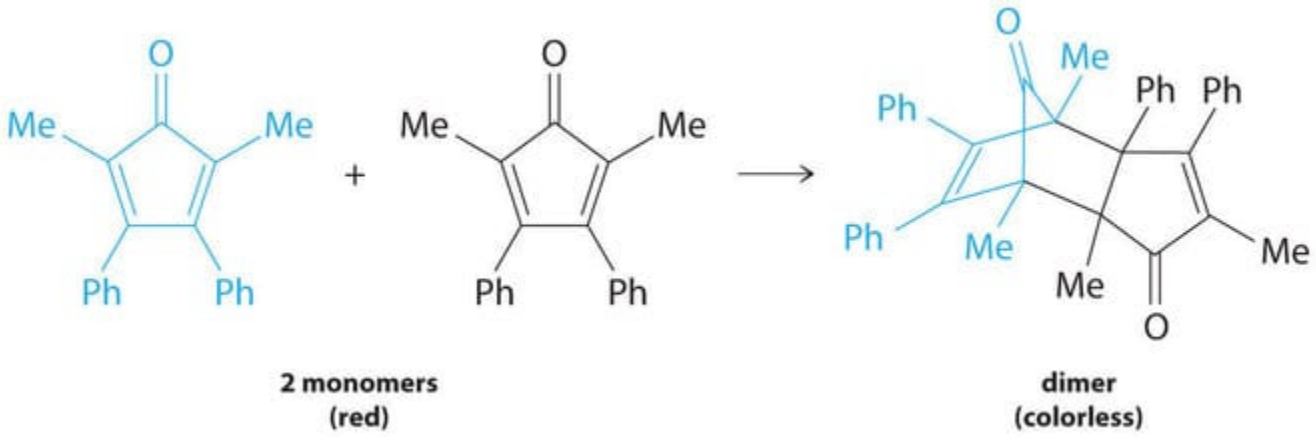


Figure 14.4.7

For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 14.4.8) or the integrated rate law (Equation 14.4.9).

Table 14.4.2: Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table 14.4.2. From the data, we see that the reaction rate is not independent of the monomer concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5}\ \text{M/min}}{1.8 \times 10^{-5}\ \text{M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3}\ \text{M}}{2.0 \times 10^{-3}\ \text{M}} = 1.7$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 14.4.8 and the data from any row in Table 14.4.2, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \tag{14.4.10}$$

$$8.0 \times 10^{-5}\ \text{M/min} = k(4.4 \times 10^{-3}\ \text{M})^2 \tag{14.4.11}$$

$$4.1\ \text{M}^{-1} \cdot \text{min}^{-1} = k \tag{14.4.12}$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in Figure 14.4.8*a*. The measurements show that the concentration of the monomer (initially 5.4×10^{-3} M) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus *t* should be a straight line, as shown in Figure 14.4.8*b*. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1\ \text{M}^{-1}\cdot\text{min}^{-1}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.

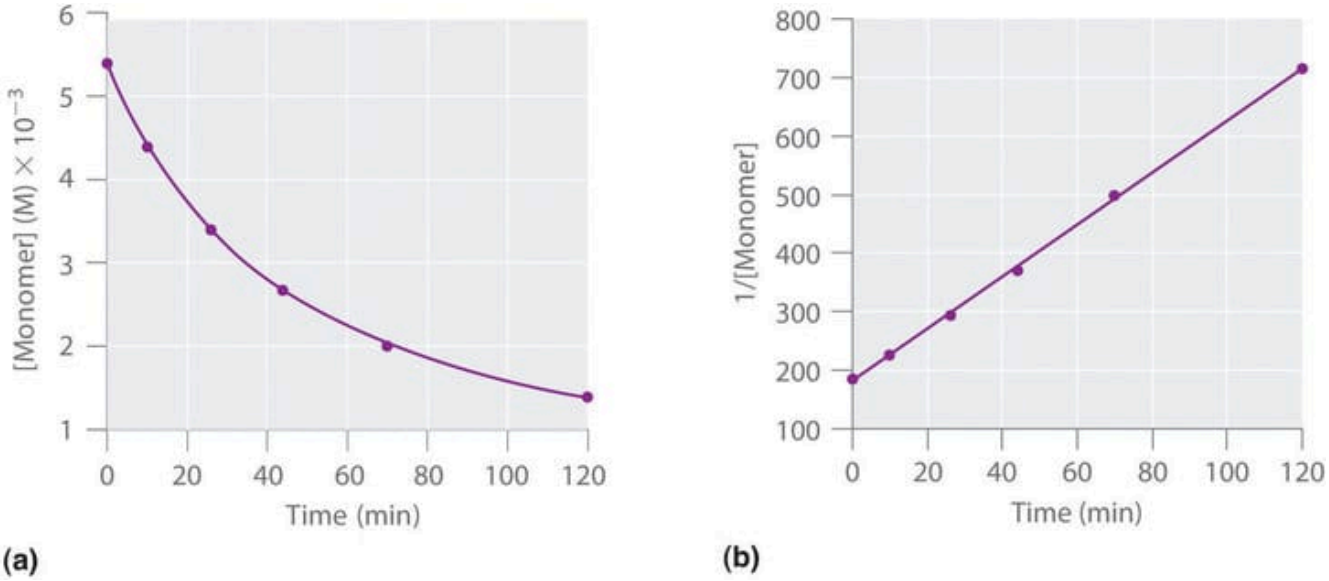


Figure 14.4.8: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.4.6 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate

constants for reactions that have different orders.

Example 14.4.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2\mathrm{NO_2(g)} \xrightarrow{\Delta} 2\mathrm{NO(g)} + \mathrm{O_2(g)}$$

Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experimental data for the reaction at 300°C and four initial concentrations of NO2

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
1	0.015	1.22×10^{-4}
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

A. From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.
B. Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (*k*).

Solution

A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO_2 concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to $[NO_2]^2$. Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to $[NO_2]^2$. This behavior is characteristic of a second-order reaction.

B We have rate = $k[NO_2]^2$. We can calculate the rate constant (*k*) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\begin{aligned} \text{rate} &= k[\mathrm{NO_2}]^2 \\ 5.40 \times 10^{-5}\ \mathrm{M/s} &= k(0.010\ \mathrm{M})^2 \\ 0.54\ \mathrm{M^{-1} \cdot s^{-1}} &= k \end{aligned}$$

Exercise 14.4.3

When the highly reactive species HO_2 forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:

$$2HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)}$$

The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Some initial rate data at 25°C

Experiment	$[HO_2]_0$ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer available at the end of this section.

If a plot of reactant concentration versus time is **not** linear, but a plot of 1/(reactant concentration) versus time is linear, then the reaction is second order.

Example 14.4.4

If a flask that initially contains 0.056 M NO_2 is heated at 300°C, what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 14.4.9) and the rate constant calculated above.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

A. Given *k*, *t*, and $[A]_0$, use the integrated rate law for a second-order reaction to calculate [A].
B. Setting [A] equal to 1/10 of $[A]_0$, use the same equation to solve for t.

Solution

A We know *k* and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at *t* = 1 h (3600 s). Substituting the appropriate values into Equation 14.4.9,

$$\begin{aligned}\frac{1}{[NO_2]_{3600}} &= \frac{1}{[NO_2]_0} + kt \\ &= \frac{1}{0.056\ \text{M}} + [(0.54\ \text{M}^{-1} \cdot \text{s}^{-1})(3600\ \text{s})] \\ &= 2.0 \times 10^3\ \text{M}^{-1}\end{aligned}$$

Thus $[NO_2]_{3600} = 5.1 \times 10^{-4}$ M.

B In this case, we know *k* and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2] = 0.1[NO_2]_0 = 0.1(0.056\ \text{M}) = 0.0056$ M. To do this, we solve Equation 14.4.9 for *t*, using the concentrations given.

$$t = \frac{(1/[\mathrm{NO_2}]) - (1/[\mathrm{NO_2}]_0)}{k}$$
$$= \frac{(1/0.0056\ \mathrm{M}) - (1/0.056\ \mathrm{M})}{0.54\ \mathrm{M^{-1} \cdot s^{-1}}}$$
$$= 3.0 \times 10^2\ \mathrm{s} = 5.0\ \mathrm{min}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Exercise 14.4.4

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9\ M^{-1}{\cdot}s^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2, calculate the concentration of HO_2 that remains after 1.0 h at 25°C. How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 14.4.9) and the rate constant calculated in the exercise in Example 14.4.3.

Answer available at the end of this section.

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form $A + B \rightarrow products$, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

$$\text{rate} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = -\frac{\Delta[\mathrm{B}]}{\Delta t} = k[\mathrm{A}][\mathrm{B}]$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.

Summary

The reaction rate of a zeroth-order reaction is independent of the concentration of the reactants. The reaction rate of a first-order reaction is directly proportional to the concentration of one reactant. The reaction rate of a simple second-order reaction is proportional to the square of the concentration of one reactant. Knowing the rate law of a reaction gives clues to the reaction mechanism.

- **zeroth-order reaction:**

$$\text{rate} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = k$$
$$[A] = [A]_0 - kt$$

- **first-order reaction**:

$$\text{rate} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}]$$
$$[A] = [A]_0 e^{-kt}$$
$$\ln[A] = \ln[A]_0 - kt$$

- **second-order reaction:**

$$\text{rate} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}]^2$$
$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt$$

Answers

Exercise 14.4.1

first order; $k = 2.2 \times 10^{-5}\ s^{-1}$

Exercise 14.4.2

0.0252 M

29 h

Exercise 14.4.3

second order in HO_2; $k = 1.4 \times 10^{9}\ M^{-1}{\cdot}s^{-1}$

Exercise 14.4.4

2.0×10^{-13} M; 6.4×10^{-6} s

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14.5: Temperature and Rate

Learning Objectives

- To understand why and how chemical reactions occur.

It is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the collision model of chemical kinetics, which is a useful tool for understanding the behavior of reacting chemical species. The collision model explains why chemical reactions often occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates. Before delving into the relationship between temperature and reaction rate, we must discuss three microscopic factors that influence the observed macroscopic reaction rates.

Microscopic Factor 1: Collisional Frequency

Central to collision model is that a chemical reaction can occur only when the reactant molecules, atoms, or ions collide. Hence, the observed rate is influence by the frequency of collisions between the reactants. The **collisional frequency** is the average rate in which two reactants collide for a given system and is used to express the average number of collisions per unit of time in a defined system. While deriving the collisional frequency (Z_{AB}) between two species in a gas is straightforward, it is beyond the scope of this text and the equation for collisional frequency of A and B is the following:

$$Z_{AB} = N_A N_B \left(r_A + r_B\right)^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}} \tag{14.5.1}$$

with

- N_A and N_B are the numbers of A and B molecules in the system, respectively
- r_a and r_b are the radii of molecule A and B, respectively
- k_B is the Boltzmann constant k_B = 1.380 x 10^{-23} Joules Kelvin
- T is the temperature in Kelvin
- μ_{AB} is calculated via $\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$

The specifics of Equation 14.5.1 are not important for this conversation, but it is important to identify that Z_{AB} increases with increasing density (i.e., increasing N_A and N_B), with increasing reactant size (r_a and r_b), with increasing velocities (predicted via Kinetic Molecular Theory), and with increasing temperature (although weakly because of the square root function).

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A Video Discussing Collision Theory of Kinetics: Collusion Theory of Kinetics (opens in new window) [youtu.be]

Microscopic Factor 2: Activation Energy

Previously, we discussed the kinetic molecular theory of gases, which showed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. What the kinetic molecular theory of gases does not explain is why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of **activation energy** (E_a). We will define this concept using the reaction of NO with ozone, which plays an important role in the depletion of ozone in the ozone layer:

$$\mathrm{NO\,(g) + O_3\,(g) \ \rightarrow NO_2\,(g) + O_2\,(g)}$$

Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

Experimental rate law for this reaction is

$$\mathrm{rate} = k[\mathrm{NO}][\mathrm{O_3}]$$

and is used to identify how the reaction rate (not the rate constant) vares with concentration. The rate constant, however, does vary with temperature. Figure $14.5.1$ shows a plot of the rate constant of the reaction of NO with $\mathrm{O_3}$ at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature (e.g, the Clausius-Claperyon equation). In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.

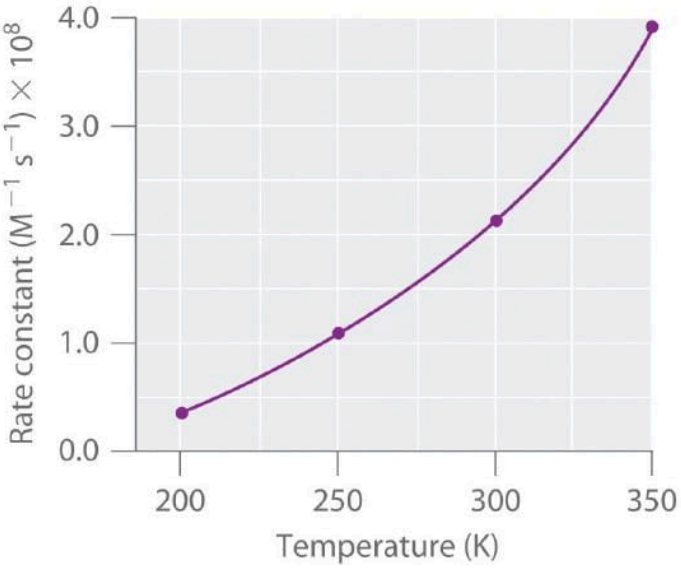


Figure $14.5.1$: Rate Constant versus Temperature for the Reaction of NO with $\mathrm{O_3}$The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases. (CC BY-SA-NC; anonymous)

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the **activation energy**, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum

amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the **activated complex** or the **transition state** of the reaction. The activated complex is not a reaction intermediate; it does not last long enough to be detected readily.

> Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure $14.5.2$ shows a plot for the $NO–O_3$ system, in which the vertical axis is potential energy and the horizontal axis is the reaction coordinate, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction (ΔE) is negative, which means that the reaction releases energy. (In this case, ΔE is –200.8 kJ/mol.) To react, however, the molecules must overcome the energy barrier to reaction (E_a is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.

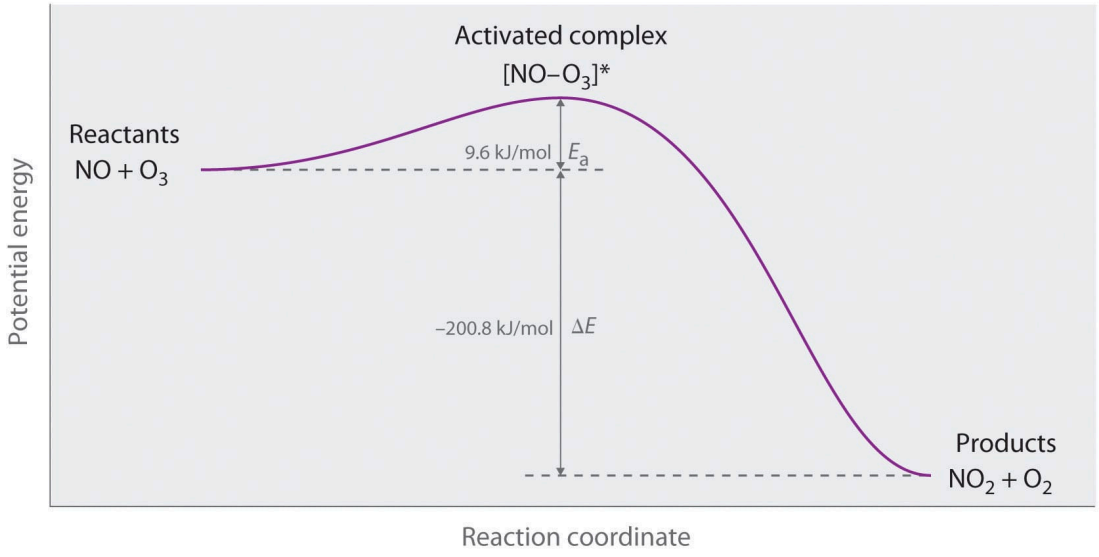


Figure $14.5.2$: Energy of the Activated Complex for the $NO–O_3$ System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex. (CC BY-SA-NC; anonymous)

Figure $14.5.3a$ illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, Figure $14.5.3b$ illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and \(\Delta E > 0\). Although the energy changes that result from a reaction can be positive, negative, or even zero, in most cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is almost always positive; there is a class of reactions called barrierless reactions, but those are discussed elsewhere.

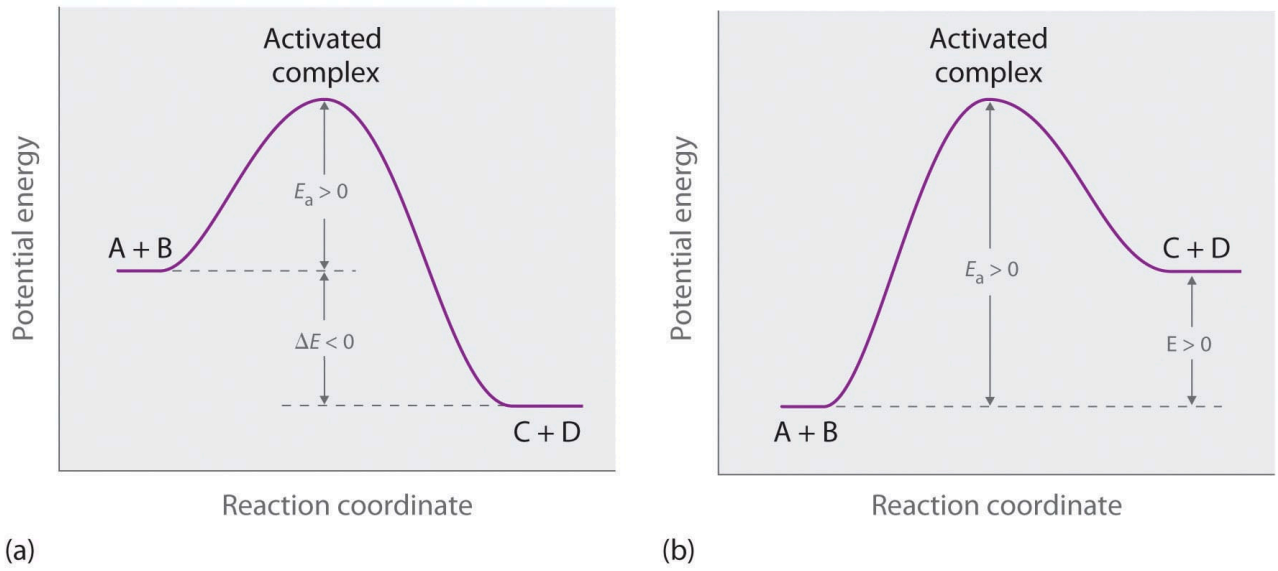


Figure 14.5.3: Differentiating between E_a and ΔE. The potential energy diagrams for a reaction with (a) ΔE < 0 and (b) ΔE > 0 illustrate the change in the potential energy of the system as reactants are converted to products. In both cases, E_a is positive. For a reaction such as the one shown in (b), E_a must be greater than ΔE. (CC BY-SA-NC; anonymous)

For similar reactions under comparable conditions, the one with the smallest E_a will occur most rapidly.

Whereas ΔE is related to the tendency of a reaction to occur spontaneously, E_a gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. For two similar reactions under comparable conditions, the reaction with the smallest E_a will occur more rapidly.

Figure 14.5.4 shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than E_a; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than E_a. Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.

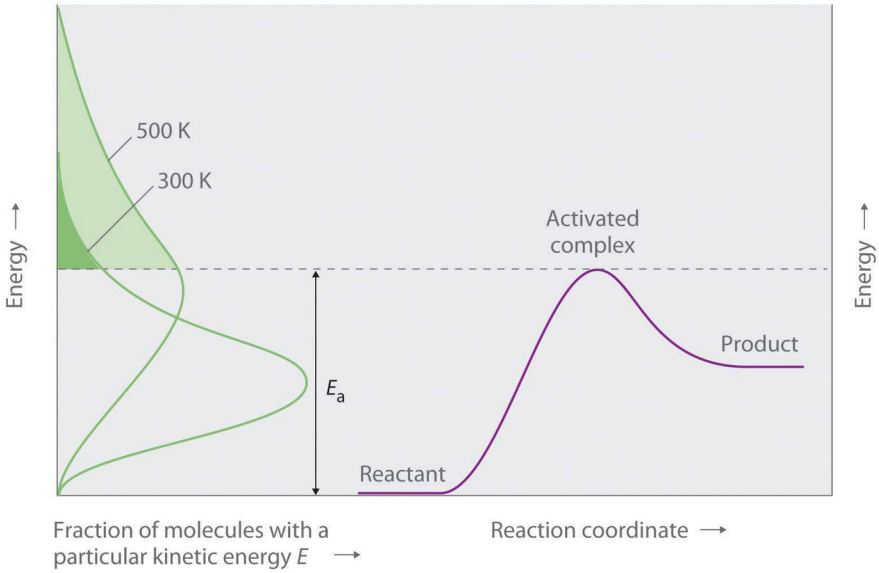


Figure 14.5.4: Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have E > E_a and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K. (CC BY-SA-NC; anonymous)

Energy is on the y axis while reaction coordinate and fraction of molecules with a particular kinetic energy E are on the x axis.

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Microscopic Factor 3: Sterics

Even when the energy of collisions between two reactant species is greater than E_a, most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and $\mathrm{O_3}$ to produce $\mathrm{NO_2}$ and $\mathrm{O_2}$, a terminal oxygen atom of $\mathrm{O_3}$ must collide with the nitrogen atom of NO at an angle that allows $\mathrm{O_3}$ to transfer an oxygen atom to NO to produce $\mathrm{NO_2}$ (Figure 14.5.4). All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and $\mathrm{O_3}$ result in a reaction at kinetic energies greater than E_a, most collisions of NO and $\mathrm{O_3}$ are unproductive. The fraction of orientations that result in a reaction is called the **steric factor** (ρ) and its value can range from $\rho = 0$ (no orientations of molecules result in reaction) to $\rho = 1$ (all orientations result in reaction).

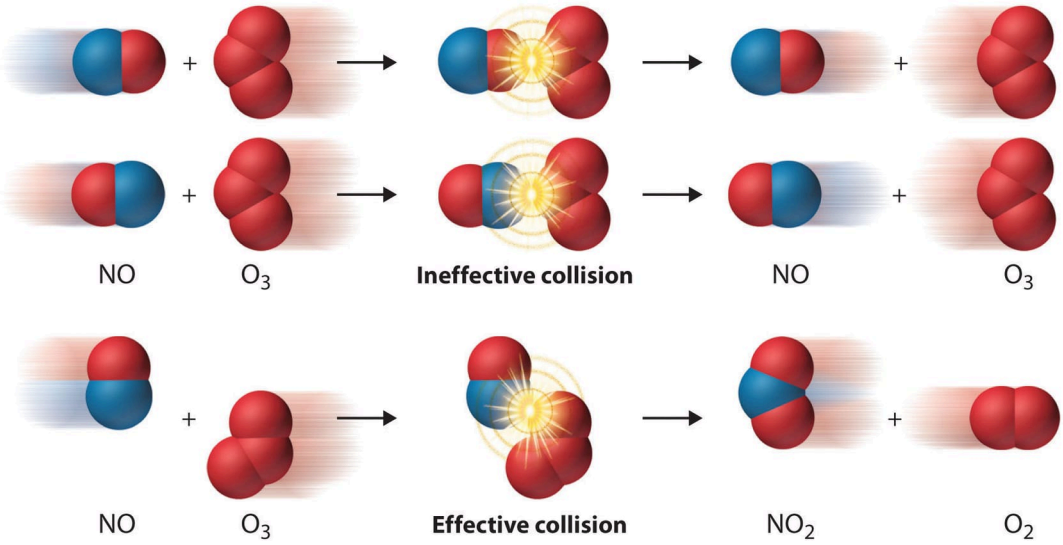


Figure 14.5.4: The Effect of Molecular Orientation on the Reaction of NO and $\mathrm{O_3}$. Most collisions of NO and $\mathrm{O_3}$ molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of $\mathrm{O_3}$ are likely to produce $\mathrm{NO_2}$ and $\mathrm{O_2}$, even if the molecules collide with $E > E_a$. (CC BY-SA-NC; anonymous)

Macroscopic Behavior: The Arrhenius Equation

The collision model explains why most collisions between molecules do not result in a chemical reaction. For example, nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about 10^{30} times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then $\mathrm{NO_2}$ a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide.

For an $A + B$ elementary reaction, all three microscopic factors discussed above that affect the reaction rate can be summarized in a single relationship:

$$\text{rate} = (\text{collision frequency}) \times (\text{steric factor}) \times (\text{fraction of collisions with } E > E_a)$$

where

$$\text{rate} = k[A][B] \tag{14.5.2}$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, A, called the **frequency factor**:

$$k = Ae^{-E_a/RT} \tag{14.5.3}$$

The frequency factor is used to convert concentrations to collisions per second (scaled by the steric factor). Because the frequency of collisions depends on the temperature, A is actually not constant (Equation 14.5.1). Instead, A increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time.

Equation 14.5.3 is known as the **Arrhenius equation** and summarizes the collision model of chemical kinetics, where T is the absolute temperature (in K) and R is the ideal gas constant [8.314 J/(K·mol)]. E_a indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large E_a increases rapidly with increasing temperature, whereas the reaction rate with a smaller E_a increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 14.5.3,

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right) \tag{14.5.4}$$

$$= \ln A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right] \tag{14.5.5}$$

Equation 14.5.5 is the equation of a straight line,

$$y = mx + b$$

where $y = \ln k$ and $x = 1/T$. This means that a plot of $\ln k$ versus $1/T$ is a straight line with a slope of $-E_a/R$ and an intercept of $\ln A$. In fact, we need to measure the reaction rate at only two temperatures to estimate E_a.

Knowing the E_a at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters. The procedure for determining E_a from reaction rates measured at several temperatures is illustrated in Example 14.5.1.

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A Video Discussing The Arrhenius Equation: The Arrhenius Equation(opens in new window) [youtu.be]

Example 14.5.1: Chirping Tree Crickets

Many people believe that the rate of a tree cricket's chirping is related to temperature. To see whether this is true, biologists have carried out accurate measurements of the rate of tree cricket chirping (f) as a function of temperature (T). Use the data in the following table, along with the graph of ln[chirping rate] versus $1/T$ to calculate E_a for the biochemical reaction that controls cricket chirping. Then predict the chirping rate on a very hot evening, when the temperature is 308 K (35°C, or 95°F).

Chirping Tree Crickets Frequency Table

Frequency (f; chirps/min)	ln f	T (K)	1/T (K)
200	5.30	299	3.34×10^{-3}
179	5.19	298	3.36×10^{-3}
158	5.06	296	3.38×10^{-3}
141	4.95	294	3.40×10^{-3}
126	4.84	293	3.41×10^{-3}
112	4.72	292	3.42×10^{-3}
100	4.61	290	3.45×10^{-3}
89	4.49	289	3.46×10^{-3}
79	4.37	287	3.48×10^{-3}

Given: chirping rate at various temperatures

Asked for: activation energy and chirping rate at specified temperature

Strategy:

A. From the plot of $\ln f$ versus $1/T$, calculate the slope of the line ($-E_a/R$) and then solve for the activation energy.
B. Express Equation 14.5.5 in terms of k_1 and T_1 and then in terms of k_2 and T_2.
C. Subtract the two equations; rearrange the result to describe k_2/k_1 in terms of T_2 and T_1.
D. Using measured data from the table, solve the equation to obtain the ratio k_2/k_1. Using the value listed in the table for k_1, solve for k_2.

Solution

A If cricket chirping is controlled by a reaction that obeys the Arrhenius equation, then a plot of $\ln f$ versus $1/T$ should give a straight line (Figure 14.5.6).

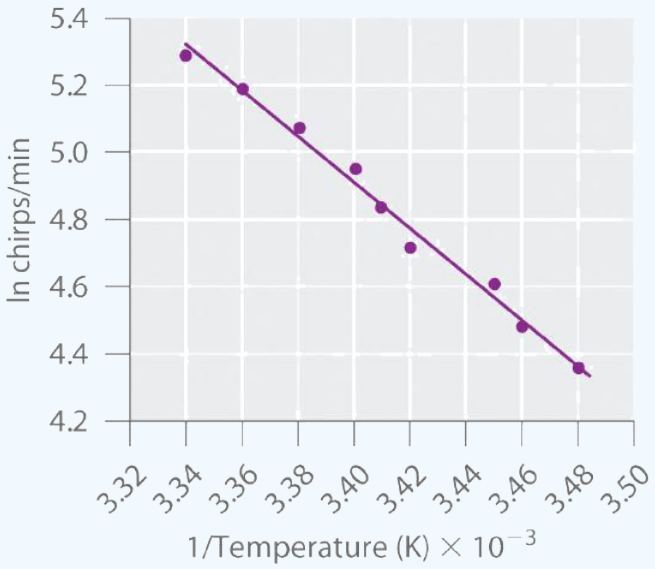


Figure 14.5.6: Graphical Determination of E_a for Tree Cricket Chirping. When the natural logarithm of the rate of tree cricket chirping is plotted versus 1/T, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an E_a of 55 kJ/mol. (CC BY-SA-NC; anonymous)

Also, the slope of the plot of $\ln f$ versus $1/T$ should be equal to $-E_a/R$. We can use the two endpoints in Figure 14.5.6 to estimate the slope:

$$\begin{aligned}\text{slope} &= \frac{\Delta \ln f}{\Delta(1/T)} \\ &= \frac{5.30 - 4.37}{3.34 \times 10^{-3}\ \text{K}^{-1} - 3.48 \times 10^{-3}\ \text{K}^{-1}} \\ &= \frac{0.93}{-0.14 \times 10^{-3}\ \text{K}^{-1}} \\ &= -6.6 \times 10^{3}\ \text{K}\end{aligned}$$

A computer best-fit line through all the points has a slope of -6.67×10^3 K, so our estimate is very close. We now use it to solve for the activation energy:

$$\begin{aligned}E_\text{a} &= -(\text{slope})(R) \\ &= -(-6.6 \times 10^{3}\ \text{K})\left(\frac{8.314\ \text{J}}{\text{K} \cdot \text{mol}}\right)\left(\frac{1\ \text{KJ}}{1000\ \text{J}}\right) \\ &= \frac{55\ \text{kJ}}{\text{mol}}\end{aligned}$$

B If the activation energy of a reaction and the rate constant at one temperature are known, then we can calculate the reaction rate at any other temperature. We can use Equation 14.5.5 to express the known rate constant (k_1) at the first temperature (T_1) as follows:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

Similarly, we can express the unknown rate constant (k_2) at the second temperature (T_2) as follows:

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

C These two equations contain four known quantities (E_a, T_1, T_2, and k_1) and two unknowns (A and k_2). We can eliminate A by subtracting the first equation from the second:

$$\begin{aligned} \ln k_2 - \ln k_1 &= \left(\ln A - \frac{E_a}{RT_2}\right) - \left(\ln A - \frac{E_a}{RT_1}\right) \\ &= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1} \end{aligned}$$

Then

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

D To obtain the best prediction of chirping rate at 308 K (T_2), we try to choose for T_1 and k_1 the measured rate constant and corresponding temperature in the data table that is closest to the best-fit line in the graph. Choosing data for T_1 = 296 K, where f = 158, and using the E_a calculated previously,

$$\begin{aligned} \ln \frac{k_{T_2}}{k_{T_1}} &= \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \\ &= \frac{55\ \text{kJ/mol}}{8.314\ \text{J/(K}\cdot\text{mol)}}\left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right)\left(\frac{1}{296\ \text{K}} - \frac{1}{308\ \text{K}}\right) \\ &= 0.87 \end{aligned}$$

Thus k_{308}/k_{296} = 2.4 and k_{308} = (2.4)(158) = 380, and the chirping rate on a night when the temperature is 308 K is predicted to be 380 chirps per minute.

Exercise 14.5.1A

The equation for the decomposition of NO_2 to NO and O_2 is second order in NO_2:

$$2\,NO_2\,(g) \longrightarrow 2\,NO\,(g) + O_2\,(g)$$

Data for the reaction rate as a function of temperature are listed in the following table. Calculate E_a for the reaction and the rate constant at 700 K.

Data for the reaction rate as a function of temperature

T (K)	k ($M^{-1}\cdot s^{-1}$)
592	522
603	755
627	1700
652	4020
656	5030

Answer available at the end of this section.

Exercise $14.5.1B$

What E_a results in a doubling of the reaction rate with a 10°C increase in temperature from 20° to 30°C?

Answer available at the end of this section.

YouTube Video

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A Video Discussing Graphing Using the Arrhenius Equation: Graphing Using the Arrhenius Equation (opens in new window) [youtu.be] (opens in new window)

Summary

For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation. The Arrhenius equation is $k = Ae^{-E_a/RT}$. A minimum energy (activation energy,vE_a) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the activated complex, or transition state, of the reaction. At a given temperature, the higher the E_a, the slower the reaction. The fraction of orientations that result in a reaction is the steric factor. The frequency factor, steric factor, and activation energy are related to the rate constant in the Arrhenius equation: $k = Ae^{-E_a/RT}$. A plot of the natural logarithm of k versus $1/T$ is a straight line with a slope of $-E_a/R$.

Answers

Exercise $14.5.1A$

E_a = 114 kJ/mol; k_{700}= 18,600 $M^{-1}{\cdot}s^{-1}$ = 1.86 × 10^4 $M^{-1}{\cdot}s^{-1}$.

Exercise $14.5.1B$

about 51 kJ/mol

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14.6: Reaction Mechanisms

Learning Objectives

- To determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the mechanism of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the reaction mechanism.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

$$2\,C_8H_{18}\,(l) + 25\,O_2\,(g) \longrightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g) \tag{14.6.1}$$

For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an **elementary reaction**, involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the **mechanism** of the reaction. The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.

> The overall sequence of elementary reactions is the mechanism of the reaction.

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

$$NO_2\,(g) + CO\,(g) \longrightarrow NO\,(g) + CO_2\,(g) \tag{14.6.2}$$

From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of NO_2 with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$rate = k[{NO_2}^2] \tag{14.6.3}$$

The fact that the reaction is second order in $[NO_2]$ and independent of $[CO]$ tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be

$$rate = k[NO_2][CO].$$

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

two-step mechanism

step 1	$NO_2 + NO_2 \xrightarrow{\text{slow}} NO_3 + NO$	elementary reaction
step 2	$\underline{NO_3 + CO \rightarrow NO_2 + CO_2}$	elementary reaction
sum	$NO_2 + CO \rightarrow NO + CO_2$	overall reaction

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The NO_3 molecule is an **intermediate** in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

The sum of the elementary reactions in a reaction mechanism **must** give the overall balanced chemical equation of the reaction.

Using Molecularity to Describe a Rate Law

The **molecularity** of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as **unimolecular**; if there are two reactant molecules, it is **bimolecular**; and if there are three reactant molecules (a relatively rare situation), it is **termolecular**. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

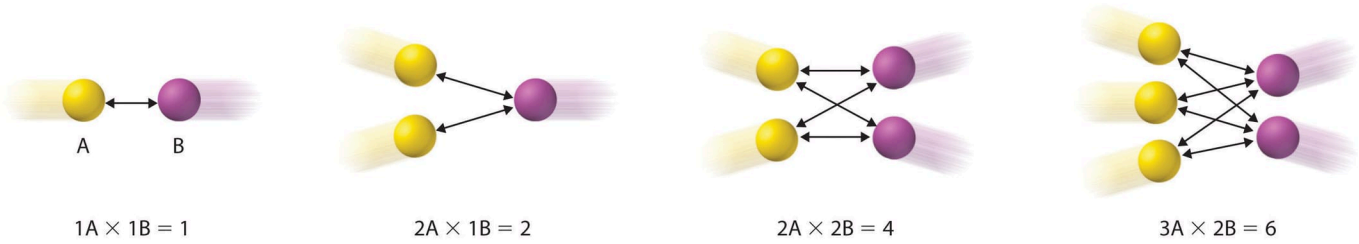


Figure 14.6.1: The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step. (CC BY-NC-SA; anonymous)

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order of the elementary reaction is the same as its molecularity (Table 14.6.1). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction (A → products) is

$$rate = k[A].$$

For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure 14.6.1. For a bimolecular elementary reaction of the form A + B → products, the general rate law is

$$rate = k[A][B].$$

Table 14.6.1: Common Types of Elementary Reactions and Their Rate Laws

Elementary Reaction	Molecularity	Rate Law	Reaction Order
A → products	unimolecular	rate = k[A]	first
2A → products	bimolecular	rate = k[A]^2	second
A + B → products	bimolecular	rate = k[A][B]	second
2A + B → products	termolecular	rate = k[A]^2[B]	third
A + B + C → products	termolecular	rate = k[A][B][C]	third

For elementary reactions, the order of the elementary reaction is the same as its molecularity. In contrast, the rate law **cannot** be determined from the balanced chemical equation for the overall reaction (unless it is a single step mechanism and is therefore also an elementary step).

Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by

which the reaction occurs, we cannot obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the slowest overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the **rate-determining step**, that must give the experimentally determined rate law for the overall reaction.This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.



Rate-determining step. The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow. (CC BY-NC-SA; anonymous)

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

rate laws for each elementary reaction in our example as well as for the overall reaction.

step 1	$\mathrm{NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO}$	$\mathrm{rate} = k_1[\mathrm{NO_2}]^2$ (predicted)
step 2	$\underline{\mathrm{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}}$	$\mathrm{rate} = k_2[\mathrm{NO_3}][\mathrm{CO}]$ (predicted)
sum	$\mathrm{NO_2 + CO \xrightarrow{k} NO + CO_2}$	$\mathrm{rate} = k[\mathrm{NO_2}]^2$ (observed)

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1. That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

Example 14.6.1: A Reaction with an Intermediate

In an alternative mechanism for the reaction of $\mathrm{NO_2}$ with CO with $\mathrm{N_2O_4}$ appearing as an intermediate.

alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} N_2O_4$
step 2	$\underline{N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2}$
sum	$NO_2 + CO \rightarrow NO + CO_2$

Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:

A. Determine the rate law for each elementary reaction in the reaction.
B. Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

Solution

A The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4, directly.

Exercise 14.6.1

Iodine monochloride (ICl) reacts with H_2 as follows:

$$2\,ICl\,(l) + H_2\,(g) \rightarrow 2\,HCl\,(g) + I_2\,(s)$$

The experimentally determined rate law is $rate = k[ICl][H_2]$. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Answer

Solutions to Exercise 14.6.1

step 1	$ICl + H_2 \xrightarrow{k_1} HCl + HI$	$\text{rate} = k_1[ICl][H_2]$ (slow)
step 2	$\underline{HI + ICl \xrightarrow{k_2} HCl + I_2}$	$\text{rate} = k_2[HI][ICl]$ (fast)
sum	$2ICl + H_2 \rightarrow 2HCl + I_2$	

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

Example 14.6.2 : Nitrogen Oxide Reacting with Molecular Hydrogen

Assume the reaction between NO and H_2 occurs via a three-step process:

the reaction between NO and $\mathrm{H_2}$ occurs via a three-step process

step 1	$\mathrm{NO + NO \xrightarrow{k_1} N_2O_2}$	(fast)
step 2	$\mathrm{N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O}$	(slow)
step 3	$\mathrm{N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O}$	(fast)

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction:

$$\text{rate} = k[\mathrm{NO}]^2[\mathrm{H_2}]? \qquad \text{(observed)}$$

Answer

- Step 1: $rate = k_1[\mathrm{NO}]^2$
- Step 2: $rate = k_2[\mathrm{N_2O_2}][\mathrm{H_2}]$
- Step 3: $rate = k_3[\mathrm{N_2O}][\mathrm{H_2}]$

The overall reaction is then

$$\mathrm{2\,NO\,(g) + 2\,H_2\,(g) \longrightarrow N_2\,(g) + 2\,H_2O\,(g)}$$

- Rate Determining Step : #2
- Yes, because the rate of formation of $[\mathrm{N_2O_2}] = k_1[\mathrm{NO}]^2$. Substituting $k_1[\mathrm{NO}]^2$ for $[\mathrm{N_2O_2}]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.

YouTube Video

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Reaction Mechanism (Slow step followed by fast step): Reaction Mechanism (Slow step Followed by Fast Step)(opens in new window) [youtu.be] (opens in new window)

Summary

A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law. A reaction mechanism is the microscopic path by which reactants are transformed into products. Each step is an elementary reaction. Species that are formed in one step and consumed in another are intermediates. Each elementary reaction can be described in terms of its *molecularity*, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the rate-determining step.

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14.7: Catalysis

Learning Objectives

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Catalysts are substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it must appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a, but the net change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is not affected by the presence of a catalyst (Figure 14.7.1). Nevertheless, because of its lower E_a, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of both the forward and the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, homogeneous catalysts, and enzymes.

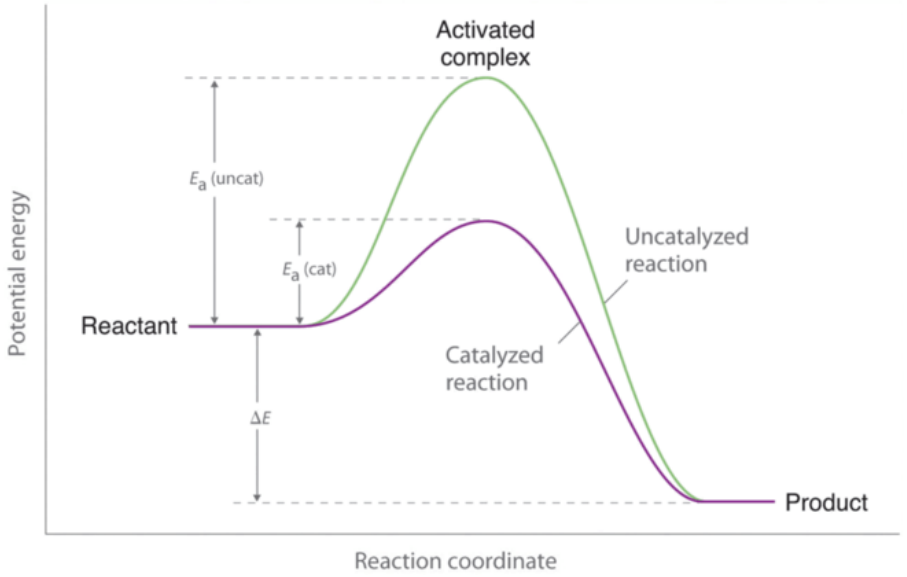


Figure 14.7.1: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE). (CC BY-NC-SA; anonymous)

The green line represents the uncatalyzed reaction. The purple line represent the catalyzed reaction .

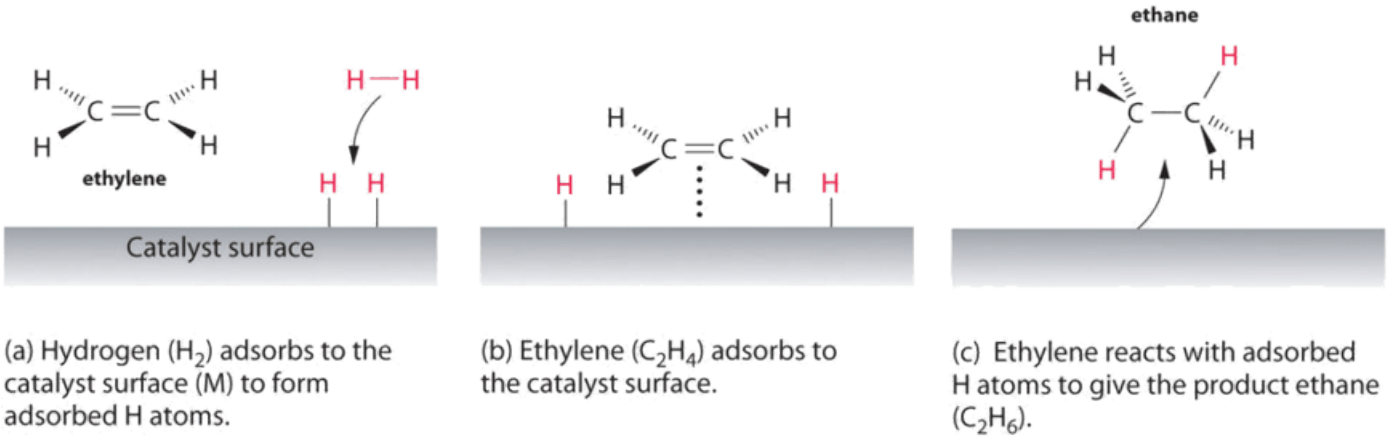
A catalyst affects E_a, not ΔE.

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 14.7.2, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy =

432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.



(a) Hydrogen (H_2) adsorbs to the catalyst surface (M) to form adsorbed H atoms.

(b) Ethylene (C_2H_4) adsorbs to the catalyst surface.

(c) Ethylene reacts with adsorbed H atoms to give the product ethane (C_2H_6).

Figure 14.7.2: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure 14.7.2 shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 14.7.1. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

Table 14.7.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

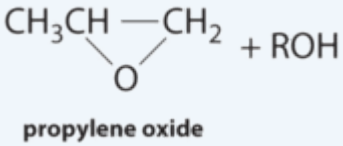
Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O$	$CH_2{=}CHCN$ acrylonitrile
catalytic hydrogenation	Ni, Pd, or Pt	RCH=CHR′ + H2 → RCH_2—CH_2R'	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In **homogeneous catalysis**, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous

catalysts in industry are transition metal compounds (Table 14.7.2), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table 14.7.2: Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	$[Rh(CO)_2I_2]^-$	$CO + CH_3OH$	CH_3CO_2H
hydroperoxide process	Mo(VI) complexes	$CH_3CH{=}CH_2 + R{-}O{-}O{-}H$	 propylene oxide
hydroformylation	Rh/PR_3 complexes	$RCH{=}CH_2 + CO + H_2$	RCH_2CH_2CHO
adiponitrile process	Ni/PR_3complexes	$2HCN + CH_2{=}CHCH{=}CH_2$	$NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon
olefin polymerization	$(RC_5H_5)_2ZrCl_2$	$CH_2{=}CH_2$	$-(CH_2CH_2-)_n$: high-density polyethylene

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a **substrate**.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37 °C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be proteases, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure 14.7.3).



Figure 14.7.3: A Catalytic Defense Mechanism. The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of H_2O_2.

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In heterogeneous catalysis, catalysts provide a surface to which reactants bind in a process of adsorption. In homogeneous catalysis, catalysts are in the same phase as the reactants. Enzymes are biological catalysts that produce large increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a substrate. Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

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14.E: Exercises

14.1: Factors that Affect Reaction Rates

Q14.1.1

What information can you obtain by studying the chemical kinetics of a reaction? Does a balanced chemical equation provide the same information? Why or why not?

S14.1.1

Kinetics gives information on the reaction rate and reaction mechanism; the balanced chemical equation gives only the stoichiometry of the reaction.

Q14.1.2

If you were tasked with determining whether to proceed with a particular reaction in an industrial facility, why would studying the chemical kinetics of the reaction be important to you?

S14.1.2

Studying chemical kinetics determines whether to proceed with a reaction as it measures the rate of a reaction. Reactions conducted in an industrial facility mix compounds together, heating and stirring them for a while, before moving to the next process. When the compounds are then moved to the next phase of the process it is important to know how long to hold the reaction at one stage before continuing, to make sure a reaction has finished before starting the next one

Q14.1.3

What is the relationship between each of the following factors and the reaction rate: reactant concentration, temperature of the reaction, physical properties of the reactants, physical and chemical properties of the solvent, and the presence of a catalyst?

S14.1.3

Reactant concentration:

Reaction rate and the concentration of reactants have a direct relationship; as concentration goes up, so does reaction rate. This is because a higher concentration causes the reactants to have a higher probability to collide with a another reactant particle, possibly inducing the chemical reaction. This comes from the Collision theory.

Reaction temperature:

Reaction rate and the reaction temperature also have a direct relationship; as temperature goes up, so does reaction rate. A higher temperature makes the particles move at a faster speed so when two or more reactant particles collide, they collide with more energy and are more likely to reach the activation energy threshold, starting a chemical reaction.

Physical properties of the reactants:

If the reactants have the same physical properties, they are more likely to react, increasing the reaction rate, because the reactants mix and are more likely to collide another one of the reactants.

Physical and chemical properties of the solvent:

The properties of the solvent also affect the rates of a reaction. High viscosity means that particles more slowly than in low viscosity solvents, so reaction rates are slower in high viscosity solvents than in low viscosity solvents. This indicates an inverse relationship between viscosity and reaction rate.

Presence of a catalyst:

The chemical definition of a catalyst in a substance that increases the rate of a reaction without being used up in the reaction. Therefore, if a catalyst is present, reaction rate increases.

Q14.1.4

A slurry is a mixture of a finely divided solid with a liquid in which it is only sparingly soluble. As you prepare a reaction, you notice that one of your reactants forms a slurry with the solvent, rather than a solution. What effect will this have on the reaction rate? What steps can you take to try to solve the problem?

Q14.1.5

Why does the reaction rate of virtually all reactions increase with an increase in temperature? If you were to make a glass of sweetened iced tea the old-fashioned way, by adding sugar and ice cubes to a glass of hot tea, which would you add first?

S14.1.5

Increasing the temperature increases the average kinetic energy of molecules and ions, causing them to collide more frequently and with greater energy, which increases the reaction rate. First dissolve sugar in the hot tea, and then add the ice.

Q14.1.6

In a typical laboratory setting, a reaction is carried out in a ventilated hood with air circulation provided by outside air. A student noticed that a reaction that gave a high yield of a product in the winter gave a low yield of that same product in the summer, even though his technique did not change and the reagents and concentrations used were identical. What is a plausible explanation for the different yields?

Q14.1.7

A very active area of chemical research involves the development of solubilized catalysts that are not made inactive during the reaction process. Such catalysts are expected to increase reaction rates significantly relative to the same reaction run in the presence of a heterogeneous catalyst. What is the reason for anticipating that the relative rate will increase?

Q14.1.8

Water has a dielectric constant more than two times greater than that of methanol (80.1 for H_2O and 33.0 for CH_3OH). Which would be your solvent of choice for a substitution reaction between an ionic compound and a polar reagent, both of which are soluble in either methanol or water? Why?

14.2: Reaction Rates

Q14.2.1

Explain why the reaction rate is generally fastest at early time intervals. For the second-order A + B → C, what would the plot of the concentration of C versus time look like during the course of the reaction?

S14.2.1

Reactant concentrations are highest at the beginning of a reaction. The plot of [C] versus t is a curve with a slope that becomes steadily less positive.

Q14.2.2

Explain the differences between a differential rate law and an integrated rate law. What two components do they have in common? Which form is preferred for obtaining a reaction order and a rate constant? Why?

Q14.2.3

Diffusion-controlled reactions have rates that are determined only by the reaction rate at which two reactant molecules can diffuse together. These reactions are rapid, with second-order rate constants typically on the order of 10^{10} L/(mol·s). Are the reactions expected to be faster or slower in solvents that have a low viscosity? Why? Consider the reactions $H_3O^+ + OH^- \rightarrow 2H_2O$ and $H_3O^+ + N(CH_3)_3 \rightarrow H_2O + HN(CH_3)_3^+$ in aqueous solution. Which would have the higher rate constant? Why?

S14.2.3

Faster in a less viscous solvent because the rate of diffusion is higher; the H_3O^+/OH^- reaction is faster due to the decreased relative size of reactants and the higher electrostatic attraction between the reactants.

Q14.2.4

What information can be obtained from the reaction order? What correlation does the reaction order have with the stoichiometry of the overall equation?

Q14.2.5

During the hydrolysis reaction $A + H_2O \rightarrow B + C$, the concentration of A decreases much more rapidly in a polar solvent than in a nonpolar solvent. How would this effect be reflected in the overall reaction order?

Q14.2.6

The reaction rate of a particular reaction in which A and B react to make C is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = \frac{1}{2}\left(\frac{\Delta[\text{C}]}{\Delta t}\right)$$

Write a reaction equation that is consistent with this rate law. What is the rate expression with respect to time if 2A are converted to 3C?

Q14.2.7

While commuting to work, a person drove for 12 min at 35 mph, then stopped at an intersection for 2 min, continued the commute at 50 mph for 28 min, drove slowly through traffic at 38 mph for 18 min, and then spent 1 min pulling into a parking space at 3 mph. What was the average rate of the commute? What was the instantaneous rate at 13 min? at 28 min?

Q14.2.8

Why do most studies of chemical reactions use the initial rates of reaction to generate a rate law? How is this initial rate determined? Given the following data, what is the reaction order? Estimate.

Time (s)	[A] (M)
120	0.158
240	0.089
360	0.062

Q14.2.9

Predict how the reaction rate will be affected by doubling the concentration of the first species in each equation.

a. $C_2H_5I \rightarrow C_2H_4 + HI$: rate = $k[C_2H_5I]$
b. $SO + O_2 \rightarrow SO_2 + O$: rate = $k[SO][O_2]$
c. $2CH_3 \rightarrow C_2H_6$: rate = $k[CH_3]^2$
d. $ClOO \rightarrow Cl + O_2$: rate = k

Q14.2.10

Cleavage of C_2H_6 to produce two CH_3· radicals is a gas-phase reaction that occurs at 700°C. This reaction is first order, with k = 5.46×10^{-4} s^{-1}. How long will it take for the reaction to go to 15% completion? to 50% completion?

S14.2.10

298 s; 1270 s

Q14.2.11

Three chemical processes occur at an altitude of approximately 100 km in Earth's atmosphere.

$$N_2^+ + O_2 \xrightarrow{k_1} N_2 + O_2^+ \tag{14.E.1}$$

$$O_2^+ + O \xrightarrow{k_2} O_2 + O^+ \tag{14.E.2}$$

$$(O^+ + N_2 \xrightarrow{k_3} NO^+ + N \tag{14.E.3}$$

Write a rate law for each elementary reaction. If the rate law for the overall reaction were found to be rate = $k[N_2^+][O_2]$, which one of the steps is rate limiting?

Q14.2.12

The oxidation of aqueous iodide by arsenic acid to give I_3^- and arsenous acid proceeds via the following reaction:

$$H_3AsO_4(aq) + 3I^-(aq) + 2H^+(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_3AsO_3(aq) + I_3^-(aq) + H_2O(l)$$

Write an expression for the initial rate of decrease of $[I_3^-]$, $\Delta[I_3^-]/\Delta t$. When the reaction rate of the forward reaction is equal to that of the reverse reaction: $k_f/k_r = [H_3AsO_3][I_3^-]/[H_3AsO_4][I^-]^3[H^+]^2$. Based on this information, what can you say about the nature of the rate-determining steps for the reverse and the forward reactions?

14.3: Concentration and Rate

14.4: The Change of Concentration with Time

Q14.4.1

What are the characteristics of a zeroth-order reaction? Experimentally, how would you determine whether a reaction is zeroth order?

Q14.4.2

Predict whether the following reactions are zeroth order and explain your reasoning.

a. a substitution reaction of an alcohol with HCl to form an alkyl halide and water
b. catalytic hydrogenation of an alkene
c. hydrolysis of an alkyl halide to an alcohol
d. enzymatic conversion of nitrate to nitrite in a soil bacterium

Q14.4.3

In a first-order reaction, what is the advantage of using the integrated rate law expressed in natural logarithms over the rate law expressed in exponential form?

Q14.4.4

If the reaction rate is directly proportional to the concentration of a reactant, what does this tell you about (a) the reaction order with respect to the reactant and (b) the overall reaction order?

Q14.4.5

The reaction of NO with O_2 is found to be second order with respect to NO and first order with respect to O_2. What is the overall reaction order? What is the effect of doubling the concentration of each reagent on the reaction rate?

Q14.4.6

Iodide reduces Fe(III) according to the following reaction:

$$2Fe^{3+}(soln) + 2I^{-}(soln) \rightarrow 2Fe^{2+}(soln) + I_2(soln) \tag{14.E.4}$$

Experimentally, it was found that doubling the concentration of Fe(III) doubled the reaction rate, and doubling the iodide concentration increased the reaction rate by a factor of 4. What is the reaction order with respect to each species? What is the overall rate law? What is the overall reaction order?

S14.4.6

First order in Fe^{3+}; second order in I^{-}; third order overall; rate = $k[Fe^{3+}][I^{-}]^2$.

Q14.4.7

Benzoyl peroxide is a medication used to treat acne. Its rate of thermal decomposition at several concentrations was determined experimentally, and the data were tabulated as follows:

Experiment	[Benzoyl Peroxide]$_0$ (M)	Initial Rate (M/s)
1	1.00	2.22×10^{-4}
2	0.70	1.64×10^{-4}
3	0.50	1.12×10^{-4}
4	0.25	0.59×10^{-4}

What is the reaction order with respect to benzoyl peroxide? What is the rate law for this reaction?

S14.4.7

The general rate law is: rate = k [Benzoyl Peroxide]^m. In order to find the reaction order with respect to benzoyl peroxide, divide two rate laws and solve for m:

$$\frac{rate_2}{rate_1} = \frac{k_2}{k_1}\left(\frac{[BenzoylPeroxide]_2}{[BenzoylPeroxide]_1}\right)^m$$

$$\frac{1.64 \times 10^{-}4\frac{M}{s}}{2.22 \times 10^{-}4\frac{M}{s}} = (\frac{0.070M}{1.00M})^m$$

$$0.738 = (0.7)^m$$

$$m = 0.85$$

rate law: rate = k [Benzoyl Peroxide]$^{0.85}$

Q14.4.8

1-Bromopropane is a colorless liquid that reacts with $S_2O_3^{2-}$ according to the following reaction:

$$C_3H_7Br + S_2O_3^{2-} \rightarrow C_3H_7S_2O_3^- + Br^- \tag{14.E.5}$$

The reaction is first order in 1-bromopropane and first order in $S_2O_3^{2-}$, with a rate constant of 8.05×10^{-4} $M^{-1}{\cdot}s^{-1}$. If you began a reaction with 40 mmol/100 mL of C_3H_7Br and an equivalent concentration of $S_2O_3^{2-}$, what would the initial reaction rate be? If you were to decrease the concentration of each reactant to 20 mmol/100 mL, what would the initial reaction rate be?

S14.4.8

1.29×10^{-4} M/s; 3.22×10^{-5} M/s

Q14.4.9

The experimental rate law for the reaction 3A + 2B → C + D was found to be $\Delta[C]/\Delta t = k[A]^2[B]$ for an overall reaction that is third order. Because graphical analysis is difficult beyond second-order reactions, explain the procedure for determining the rate law experimentally.

14.5: Temperature and Rate

Q14.5.1

Although an increase in temperature results in an increase in kinetic energy, this increase in kinetic energy is not sufficient to explain the relationship between temperature and reaction rates. How does the activation energy relate to the chemical kinetics of a reaction? Why does an increase in temperature increase the reaction rate despite the fact that the average kinetic energy is still less than the activation energy?

S14.5.1

Activation energy is required for a collision between molecules to result in a chemical reaction, as well it is related to the rate due to the Arrhenius equation

Activation energy is the threshold of energy needed in order for a reaction to occur. Reactant particles must collide with enough energy to be able to break chemical bonds, that will then allow the creation of new bonds. If the particles do not have enough energy, when they collide they will simply bounce off one another.

$k=Ae^{(-Ea/RT)}$. The increase in temperature increases the rate of reaction despite the fact the average kinetic is less than the activation energy since it increase the rate of collision between molecules.

With an increase in temperature, there is a greater distribution of kinetic energy among reactant particles. This increase of temperature allows the rate in which particles collide with one another to increase. Although the average kinetic energy is still lower than the activation energy, the increase of collisions among particles increases the chance of particles that contain enough energy to overcome the energy barrier to collide. Thus, the reaction rate increases due to this increased rate of collisions.

Additionally, there is a higher amount of molecules that have sufficient kinetic energy to overcome the energy barrier, despite the average energy of all these molecules still being lower than the activation energy.

Q14.5.2

For any given reaction, what is the relationship between the activation energy and each of the following?

a. electrostatic repulsions
b. bond formation in the activated complex
c. the nature of the activated complex

S14.5.2

1.) Electrostatic repulsion: Electrostatic repulsion is the unfavorable interaction between two species of like charge. Activation energy is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed.

2.) Bond formation in the activated complex: An activated complex is an intermediate state that is formed during the conversion of reactants into products. Bond breaking can increase activation energy as breaking bonds requires energy.

3.) Nature of the activated complex: The activation energy of a chemical reaction is the difference between the energy of the activated complex and the energy of the reactants. If the structure has a high steric hindrance the activation energy will be higher.

Q14.5.3

If you are concerned with whether a reaction will occur rapidly, why would you be more interested in knowing the magnitude of

the activation energy than the change in potential energy for the reaction?

Q14.5.4

The product C in the reaction A + B → C + D can be separated easily from the reaction mixture. You have been given pure A and pure B and are told to determine the activation energy for this reaction to determine whether the reaction is suitable for the industrial synthesis of C. How would you do this? Why do you need to know the magnitude of the activation energy to make a decision about feasibility?

Q14.5.5

Above E_a, molecules collide with enough energy to overcome the energy barrier for a reaction. Is it possible for a reaction to occur at a temperature less than that needed to reach E_a? Explain your answer.

Q14.5.6

What is the relationship between A, E_a, and T? How does an increase in A affect the reaction rate?

Q14.5.7

Of two highly exothermic reactions with different values of E_a, which would need to be monitored more carefully: the one with the smaller value or the one with the higher value? Why?

Q14.5.8

What happens to the approximate rate of a reaction when the temperature of the reaction is increased from 20°C to 30°C? What happens to the reaction rate when the temperature is raised to 70°C? For a given reaction at room temperature (20°C), what is the shape of a plot of reaction rate versus temperature as the temperature is increased to 70°C?

S14.5.8

The reaction rate will approximately double: 20°C to 30°C, the reaction rate increases by about $2^1 = 2$; 20°C to 70°C, the reaction rate increases by about $2^5 = 32$-fold. A plot of reaction rate versus temperature will give an exponential increase: rate $\propto 2^{\Delta T/10}$.

Q14.5.9

Acetaldehyde, used in silvering mirrors and some perfumes, undergoes a second-order decomposition between 700 and 840 K. From the data in the following table, would you say that acetaldehyde follows the general rule that each 10 K increase in temperature doubles the reaction rate?

T (K)	k ($M^{-1}\cdot s^{-1}$)
720	0.024
740	0.051
760	0.105
800	0.519

Q14.5.10

Bromoethane reacts with hydroxide ion in water to produce ethanol. The activation energy for this reaction is 90 kJ/mol. If the

reaction rate is 3.6×10^{-5} M/s at 25°C, what would the reaction rate be at the following temperatures?

a. 15°C
b. 30°C
c. 45°C

Q14.5.11

An enzyme-catalyzed reaction has an activation energy of 15 kcal/mol. How would the value of the rate constant differ between 20°C and 30°C? If the enzyme reduced the E_a from 25 kcal/mol to 15 kcal/mol, by what factor has the enzyme increased the reaction rate at each temperature?

S14.5.11

a. 1.0×10^{-5} M/s
b. 6.6×10^{-5} M/s
c. 3.5×10^{-4} M/s

Q14.5.12

The data in the following table are the rate constants as a function of temperature for the dimerization of 1,3-butadiene. What is the activation energy for this reaction?

T (K)	k ($M^{-1} \cdot min^{-1}$)
529	1.4
560	3.7
600	25
645	82

S14.5.12

100 kJ/mol

Q14.5.13

The reaction rate at 25°C is 1.0×10^{-4} M/s. Increasing the temperature to 75°C causes the reaction rate to increase to 7.0×10^{-2} M/s. Estimate E_a for this process. If E_a were 25 kJ/mol and the reaction rate at 25°C is 1.0×10^{-4} M/s, what would be the reaction rate at 75°C?

14.6: Reaction Mechanisms

Q14.6.1

How does the term molecularity relate to elementary reactions? How does it relate to the overall balanced chemical equation?

Q14.6.2

What is the relationship between the reaction order and the molecularity of a reaction? What is the relationship between the reaction order and the balanced chemical equation?

Q14.6.3

When you determine the rate law for a given reaction, why is it valid to assume that the concentration of an intermediate does not change with time during the course of the reaction?

Q14.6.3

If you know the rate law for an overall reaction, how would you determine which elementary reaction is rate determining? If an intermediate is contained in the rate-determining step, how can the experimentally determined rate law for the reaction be derived from this step?

Q14.6.4

Give the rate-determining step for each case.

a. Traffic is backed up on a highway because two lanes merge into one.
b. Gas flows from a pressurized cylinder fitted with a gas regulator and then is bubbled through a solution.
c. A document containing text and graphics is downloaded from the Internet.

Q14.6.5

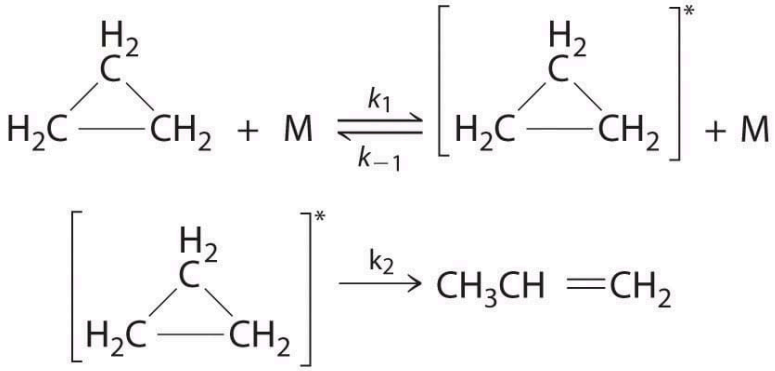
Before being sent on an assignment, an aging James Bond was sent off to a health farm where part of the program's focus was to purge his body of radicals. Why was this goal considered important to his health?

S14.6.5

Free radicals are uncharged molecules with an unpaired valence electron. The reason these are so dangerous is because they like to grab electrons from other atoms to fill their own outer shell. This allows them to impair protein function because free radicals readily oxidize proteins and cell membrane which could lead to a loss of function. It was important to purge James Bond of radicals because radicals set off chain reactions of continuously pulling electrons from molecules, which in turn, can damage cells in the body.

Q14.6.6

Cyclopropane, a mild anesthetic, rearranges to propylene via a collision that produces and destroys an energized species. The important steps in this rearrangement are as follows:



where M is any molecule, including cyclopropane. Only those cyclopropane molecules with sufficient energy (denoted with an asterisk) can rearrange to propylene. Which step determines the rate constant of the overall reaction?

S14.6.6

When we are trying to decide which step is a rate-determining step, you have to look at which step is the slowest of them all, since we have no knowledge of the time scale for either of these steps we have to look elsewhere to determine the rate-determining step.

In our specific problem, we do not know what exact molecules we have however we do see that the first step is an equilibrium since it has a double-headed arrow with two k values one that is the reciprocal of the other. Since it is an equilibrium we can reasonably assume that energized propane is rapidly created which would lead us to the conclusion that the second step is the slower of the two steps and is, therefore, the rate-determining step. So, the second step (with k_2) determines the rate constant of the overall reaction.

Q14.6.7

Above approximately 500 K, the reaction between NO_2 and CO to produce CO_2 and NO follows the second-order rate law $\Delta[CO_2]/\Delta t = k[NO_2][CO]$. At lower temperatures, however, the rate law is $\Delta[CO_2]/\Delta t = k'[NO_2]^2$, for which it is known that NO_3 is an intermediate in the mechanism. Propose a complete low-temperature mechanism for the reaction based on this rate law. Which step is the slowest?

S14.6.7

Given that NO_3 is an intermediate in the low temperature reaction mechanism, we automatically know two things: 1) *NO_3 won't show up in the final overall reaction*, and thus, 2) *NO_3 will be in the products of the first reaction of the mechanism and in the reactants of the second reaction*. We can also assume that since we're given an intermediate from the problem, this is the only intermediate (so we won't have to dream up any other compounds that might exist in the series of reactions.) These things being said, the **lower temperature reaction mechanism** will look like this:

$$2NO_2(g) \rightarrow NO_3(g) + NO(g) \tag{1}$$

$$CO(g) + NO_3(g) \rightarrow CO_2(g) + NO_2(g) \tag{2}$$

And the overall reaction will look like this (notice how NO_3 is not present):

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g) \qquad \text{(overall reaction)}$$

Now that we have the reaction mechanism written out, we can go about determining which step is the slowest. It would be pretty tricky to do this if we weren't given any further information, however, we know two more things: 1) *the high-temperature mechanism's rate = k[NO_2][CO] meaning that it took place in one step* (given that the overall reaction is also equal to this rate) and 2) *the low-temperature mechanism's rate = k'[NO_2]^2*. These two things being said, we've both confirmed that our proposed low-temperature reaction mechanism is in fact two steps, and that *we have a means to find which step is slower*.

By using the "guess-and-check" method we can label each step reaction one at a time as the **"slow reaction"** and see if the rate matches up with the rate given to us.

Let's first try the 2nd reaction. (see above)

By using rate laws we can determine that the rate of the reaction must be in terms of its reactants, which follows:

$$\mathrm{k[CO][NO_3]} \tag{14.E.6}$$

... *But wait!* We can't have the overall reaction rate in terms of an intermediate.

By looking at the 1st reaction, we can determine that we can sub in "[NO_2] /[NO]" for "[NO_3]" since by writing the full reaction rate of the first step and solving for [NO_3] this is equivalent. So, we now have the overall rate of the mechanism as the following given the 2nd reaction is the "slow reaction:"

$$\mathrm{k}\frac{[\mathrm{CO}][\mathrm{NO_2}]^2}{[\mathrm{NO}]} \tag{14.E.7}$$

Note that NO_2 is raised to the second power to account for the stoichiometry of the balanced reaction.

So clearly the 2nd reaction isn't the slow reaction since the rate is not equivalent to what we were given!

Let's check the rate of the 1st reaction now...

$$\mathrm{k}[\mathrm{NO_2}]^2 \tag{14.E.8}$$

What do you know... the rates are equal!

We have now confirmed that the 1st reaction is the slow reaction equation, since its rate is equivalent to the overall reaction rate.

Q14.6.8

Nitramide (O_2NNH_2) decomposes in aqueous solution to N_2O and H_2O. What is the experimental rate law ($\Delta[N_2O]/\Delta t$) for the decomposition of nitramide if the mechanism for the decomposition is as follows?

$\mathrm{O_2NNH_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{O_2NNH^-} + \mathrm{H^+}$	(fast)
$\mathrm{O_2NNH^-} \xrightarrow{k_2} \mathrm{N_2O} + \mathrm{OH^-}$	(slow)
$\mathrm{H^+} + \mathrm{OH^-} \xrightarrow{k_3} \mathrm{H_2O}$	(fast)

Assume that the rates of the forward and reverse reactions in the first equation are equal.

S14.6.8

We know that the slowest step of the reaction is the rate determining step, since it usually has the highest activation energy requirement. As a result, the slowest step of the reaction is the experimental rate law we are looking for.

Note: since the slowest step is the rate determining step, that usually means there is some intermediate in between. Intermediates should NEVER be a part of the rate law mechanism.

$$rate = rate_2 = k_2[O_2NNH^-] \tag{14.E.9}$$

Since Nitramide is an intermediate, we must find some way to substitute it. To solve that problem, we look for where Nitramide is produced and consumed. We see that

$$rate_1 = k_1[O_2NNH_2] \tag{14.E.10}$$

$$rate_{-1} = k_{-1}[O_2NNH^-][H^+] \tag{14.E.11}$$

Since these two rates produce and consume the same amount of O_2NNH^- over the same time period, we can set them equal to each other and solve for the intermediate

$$rate_1 = rate_{-1} \tag{14.E.12}$$

$$k_1[O_2NNH_2] = k_{-1}[O_2NNH^-][H^+] \tag{14.E.13}$$

$$[O_2NNH^-] = \frac{k_1[O_2NNH_2]}{k_{-1}[H^+]} \tag{14.E.14}$$

Substituting this equation back into our original equation gives us

$$rate = rate_2 = k_2 \frac{k_1[O_2NNH_2]}{k_{-1}[H^+]} \tag{14.E.15}$$

With all of the rate constants (k), we can clean up our equation a little bit by saying

$$k = \frac{k_2 k_1}{k_{-1}} \tag{14.E.16}$$

Leaving us with

$$rate = \frac{k[O_2NNH_2]}{[H^+]} \tag{14.E.17}$$

A14.6.8

$$\text{rate} = k_2 \frac{k_1[\text{O}_2\text{NNH}_2]}{k_{-1}[\text{H}^+]} = k\frac{[\text{O}_2\text{NNH}_2]}{[\text{H}^+]}$$

Q14.6.9

The following reactions are given:

$$\text{A} + \text{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{C} + \text{D} \tag{14.E.18}$$

$$\text{D} + \text{E} \xrightarrow{k_2} \text{F} \tag{14.E.19}$$

What is the relationship between the relative magnitudes of k_{-1} and k_2 if these reactions have the following rate law?

$$\frac{\Delta[F]}{\Delta t} = k\frac{[A][B][E]}{[C]} \tag{14.E.20}$$

How does the magnitude of k_1 compare to that of k_2? Under what conditions would you expect the rate law to be

$$\frac{\Delta[F]}{\Delta t} = k'[A][B]? \tag{14.E.21}$$

Assume that the rates of the forward and reverse reactions in the first equation are equal.

S14.6.9

First, because we have broken the equations down into elementary steps we can write the rate laws for each step.

Step1:

$$A + B \xrightarrow{k_1} C + D \tag{14.E.22}$$

$$rate = k_1[A][B] \tag{14.E.23}$$

Step 2:

$$C + D \xrightarrow{k_{-1}} A + B \tag{14.E.24}$$

$$rate = k_{-1}[C][D] \tag{14.E.25}$$

Step 3:

$$D + E \xrightarrow{k_2} F \tag{14.E.26}$$

$$rate = k_2[D][E] \tag{14.E.27}$$

If we add a these steps together we see that we get overall reaction

$$A + B + E \rightarrow C + F \tag{14.E.28}$$

we can see that [D] is an intermediate and

$$k_1 = k_{-1} \tag{14.E.29}$$

.

Since we are not told which steps are fast or slow we need to use Steady State Approximation.

If the second step is the slower step ($k_{-1} >> k_2$) then our rate determining step would be

$$rate = k_2[D][E] \tag{14.E.30}$$

Since we can only write rate laws in terms of products and reactants we have to rewrite this so that we are not including an intermediate.

Assume: rate of [D] formation = rate of its disappearance

$$k_1[A][B] = k_{-1}[C][D] + k_2[D][E] \tag{14.E.31}$$

$$k_1[A][B] = [D](k_{-1}[C] + k_2[E]) \tag{14.E.32}$$

Solving for [D] we find that

$$[D] = \frac{k_1[A][B]}{(k_{-1}[C] + k_2[E])} \tag{14.E.33}$$

now we can use this to substitute the intermediate [D] in the rate law to get an appropriate rate law.

$$rate = \frac{k_2 k_1[A][B][E]}{(k_{-1}[C] + k_2[E])} \tag{14.E.34}$$

because we had already established $k_{-1} >> k_2$ *we can assume that*

$$k_{-1}[C] + k_2[E] \approx k_{-1}[C] \tag{14.E.35}$$

this would give us the observed rate law

$$\frac{\Delta[F]}{\Delta t} = \frac{k_2 k_1[A][B][E]}{k_{-1}[C]} \tag{14.E.36}$$

to make this clearer we can set

$$k = \frac{(k_2)(k_1)}{(k_{-1})} \tag{14.E.37}$$

and we can then simplify it down to

$$\frac{\Delta[F]}{\Delta t} = k\frac{[A][B][E]}{[C]} \tag{14.E.38}$$

we can see that all of these rate constants are related by this ratio k_2k_1/k_{-1}. Since k_2 is our rate determining step $k_{-1} >> k_2$ *and since* $k_1 = k_{-1}$ then we can see that $k_1 >> k_2$.

We would expect the rate law to be

$$\frac{\Delta[F]}{\Delta t} = k'[A][B]? \tag{14.E.39}$$

if the rate determining step aka the slowest step is that corresponding to (step 1) since the rate law for this step is k_1[A][B] and

this is the exact the same as the rate law that we were given.

14.7: Catalysis

Q14.7.1

What effect does a catalyst have on the activation energy of a reaction? What effect does it have on the frequency factor (*A*)? What effect does it have on the change in potential energy for the reaction?

S14.7.1

A catalyst lowers the activation energy of a reaction. Some catalysts can also orient the reactants and thereby increase the frequency factor. Catalysts have no effect on the change in potential energy for a reaction.

Q14.7.2

How is it possible to affect the product distribution of a reaction by using a catalyst?

Q14.7.3

A heterogeneous catalyst works by interacting with a reactant in a process called *adsorption*. What occurs during this process? Explain how this can lower the activation energy.

S14.7.3

In adsorption, a reactant binds tightly to a surface. Because intermolecular interactions between the surface and the reactant weaken or break bonds in the reactant, its reactivity is increased, and the activation energy for a reaction is often decreased.

Q14.7.4

What effect does increasing the surface area of a heterogeneous catalyst have on a reaction? Does increasing the surface area affect the activation energy? Explain your answer.

Q14.7.5

Identify the differences between a heterogeneous catalyst and a homogeneous catalyst in terms of the following.

a. ease of recovery
b. collision frequency
c. temperature sensitivity
d. cost

S14.7.4

a. Heterogeneous catalysts are easier to recover.
b. Collision frequency is greater for homogeneous catalysts.
c. Homogeneous catalysts are often more sensitive to temperature.
d. Homogeneous catalysts are often more expensive.

Q14.7.6

An area of intensive chemical research involves the development of homogeneous catalysts, even though homogeneous

catalysts generally have a number of operational difficulties. Propose one or two reasons why a homogenous catalyst may be preferred.

S14.7.6

Catalysts are compounds that, when added to chemical reactions, reduce the activation energy and increase the reaction rate. The amount of a catalyst does not change during a reaction, as it is not consumed as part of the reaction process. Catalysts lower the energy required to reach the transition state of the reaction, allowing more molecular interactions to achieve that state. However, catalysts do not affect the degree to which a reaction progresses. In other words, though catalysts affect reaction kinetics, the equilibrium state remains unaffected.

Catalysts can be classified into two types: homogenous and heterogeneous. Homogenous catalysts are those which exist in the same phase (gas or liquid) as the reactants, while heterogeneous catalysts are not in the same phase as the reactants. Typically, heterogeneous catalysis involves the use of solid catalysts placed in a liquid reaction mixture. For this question, we will be discussing homogenous catalysts.

Most of the times, homogeneous catalysis involves the introduction of an aqueous phase catalyst into an aqueous solution of reactants. One reason why homogeneous catalysts are preferred over heterogeneous catalysts because homogeneous catalysts mix well in chemical reactions in comparison to heterogeneous catalysts. However, homogeneous catalyst is often irrecoverable after the reaction has run to completion.

Q14.7.7

Consider the following reaction between cerium(IV) and thallium(I) ions:

$$2\,\mathrm{Ce^{4+}} + \mathrm{Tl^{+}} \longrightarrow 2\,\mathrm{Ce^{3+}} + \mathrm{Tl^{3+}} \tag{14.E.40}$$

This reaction is slow, but Mn^{2+} catalyzes it, as shown in the following mechanism:

$$\mathrm{Ce^{4+}} + \mathrm{Mn^{2+}} \longrightarrow \mathrm{Ce^{3+}} + \mathrm{Mn^{3+}} \tag{14.E.41}$$

$$\mathrm{Ce^{4+}} + \mathrm{Mn^{3+}} \longrightarrow \mathrm{Ce^{3+}} + \mathrm{Mn^{4+}} \tag{14.E.42}$$

$$\mathrm{Mn^{4+}} + \mathrm{Tl^{+}} \longrightarrow \mathrm{Tl^{3+}} + \mathrm{Mn^{2+}} \tag{14.E.43}$$

In what way does Mn^{2+} increase the reaction rate?

S14.7.7

The Mn^{2+} ion donates two electrons to Ce^{4+}, one at a time, and then accepts two electrons from Tl^{+}. Because Mn can exist in three oxidation states separated by one electron, it is able to couple one-electron and two-electron transfer reactions.

Q14.7.8

The text identifies several factors that limit the industrial applications of enzymes. Still, there is keen interest in understanding how enzymes work for designing catalysts for industrial applications. Why?

S14.7.8

Enzymes are expensive to make, denature and fail at certain temperatures, are not that stable in a solution, and are very specific to the reaction it was made for. However, scientists can use the observations from enzymes to create catalysts that are more effective in aiding the reaction and cost less to produce. Overall, catalysts still play a large part in lowering the activation energy for reactions. Creating new catalysts can help in the improvement of areas such as medical, ecological, and even commercial products.

Q14.7.9

Most enzymes have an optimal pH range; however, care must be taken when determining pH effects on enzyme activity. A decrease in activity could be due to the effects of changes in pH on groups at the catalytic center or to the effects on groups located elsewhere in the enzyme. Both examples are observed in chymotrypsin, a digestive enzyme that is a protease that hydrolyzes polypeptide chains. Explain how a change in pH could affect the catalytic activity due to (a) effects at the catalytic center and (b) effects elsewhere in the enzyme. (*Hint*: remember that enzymes are composed of functional amino acids.)

Q14.7.10

At some point during an enzymatic reaction, the concentration of the activated complex, called an enzyme–substrate complex (ES), and other intermediates involved in the reaction is nearly constant. When a single substrate is involved, the reaction can be represented by the following sequence of equations:

$$\text{enzyme (E)} + \text{substrate (S)} \rightleftharpoons \text{enzyme-substrate complex (ES)} \rightleftharpoons \text{enzyme (E)} + \text{product (P)} \tag{14.E.44}$$

This can also be shown as follows:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P \tag{14.E.45}$$

Using molar concentrations and rate constants, write an expression for the rate of disappearance of the enzyme–substrate complex. Typically, enzyme concentrations are small, and substrate concentrations are high. If you were determining the rate law by varying the substrate concentrations under these conditions, what would be your apparent reaction order?

S14.7.10

$\frac{\Delta[ES]}{\Delta t} = -(k_2 + k_{-1})[ES] + k_1[E][S] + k_{-2}[E][P] \approx 0$; zeroth order in substrate.

Q14.7.11

A particular reaction was found to proceed via the following mechanism:

- $A + B \rightarrow C + D$ (slow)
- $2C \rightarrow E$ (fast)
- $E + A \rightarrow B + F$ (fast)

What is the overall reaction? Is this reaction catalytic, and if so, what species is the catalyst? Identify the intermediates

Q14.7.12

A particular reaction has two accessible pathways (A and B), each of which favors conversion of *X* to a different product (*Y* and *Z*, respectively). Under uncatalyzed conditions pathway A is favored, but in the presence of a catalyst pathway B is favored. Pathway B is reversible, whereas pathway A is not. Which product is favored in the presence of a catalyst? without a catalyst? Draw a diagram illustrating what is occurring with and without the catalyst.

S14.7.12

In both cases, the product of pathway A is favored. All of the *Z* produced in the catalyzed reversible pathway B will eventually be converted to *X* as *X* is converted irreversibly to *Y* by pathway A.

Q14.7.13

The kinetics of an enzyme-catalyzed reaction can be analyzed by plotting the reaction rate versus the substrate concentration. This type of analysis is referred to as a Michaelis–Menten treatment. At low substrate concentrations, the plot shows behavior

characteristic of first-order kinetics, but at very high substrate concentrations, the behavior shows zeroth-order kinetics. Explain this phenomenon.

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14.S: Chemical Kinetics (Summary)

These is a summary of key concepts of the chapter in the Textmap created for "Chemistry: The Central Science" by Brown et al.

14.1: Factors that Affect Reaction Rates

chemical kinetics – area of chemistry dealing with speeds/rates of reactions

- rates of reactions affected by four factors
  1. concentrations of reactants
  2. temperature at which reaction occurs
  3. presence of a catalyst
  4. surface area of solid or liquid reactants and/or catalysts

14.2: Reaction Rates

- **reaction rate** – speed of a chemical reaction

Misplaced '#'

$$\Delta moles\ B = moles\ B\ at\ final\ time - moles\ B\ at\ initial\ time$$

$$average\ rate = -\frac{\Delta moles\ A}{\Delta t}\ if\ A \rightarrow B$$

14.2.1 Rates in Terms of Concentrations

- rate calculated in units of M/s
- brackets around a substance indicate the concentration
- **instantaneous rate** – rate at a particular time
- instantaneous rate obtained from the straight line tangent that touches the curve at a specific point
- slopes give instantaneous rates
- instantaneous rate also referred to as the rate

14.2.2 Reaction Rates and Stoichiometry

- for the irreversible reaction $aA + bB \rightarrow cC + dD$

$$rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

14.3: Concentration and Rate

- equation used only if C and D only substances formed
- Rate = k[A][B]
- **Rate law** – expression that shows that rate depends on concentrations of reactants
- k = rate constant

14.3.1 Reaction Order

- Rate = k[reactant 1]^m[reactant 2]^n
- m, n are called reaction orders
- m+n, overall reaction order

- reaction orders do not have to correspond with coefficients in balanced equation
- values of reaction order determined experimentally
- reaction order can be fractional or negative

14.3.2 Units of Rates Constants

- units of rate constant depend on overall reaction order of rate law
- for reaction of second order overall
- units of rate = (units of rate constant)(units of concentration)^2
- units of rate constant = $M^{-1}s^{-1}$

14.3.3 Using Initial Rates to Determine Rate Laws

- **zero order** – no change in rate when concentration changed
- **first order** – change in concentration gives proportional changes in rate
- **second order** – change in concentration changes rate by the square of the concentration change, such as 2^2 or 3^2, etc...
- rate constant does not depend on concentration

14.4: The Change of Concentration with Time

- rate laws can be converted into equations that give concentrations of reactants or products

14.4.1 First-Order Reactions

$$rate = -\frac{\Delta[A]}{\Delta t} = k[A]$$

and in integral form:

$$\ln [A]_t - \ln [A]_0 = -kt$$

or

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln [A]_t = -kt + \ln [A]_0$$

- corresponds to a straight line with $y = mx + b$
- equations used to determine:
  1. concentration of reactant remaining at any time
  2. time required for given fraction of sample to react
  3. time required for reactant concentration to reach a certain level

14.3.2 Half-Life

- half-life of first order reaction

$$t_{\frac{1}{2}} = -\frac{\ln \frac{1}{2}}{k} = \frac{0.693}{k}$$

- **half-life** – time required for concentration of reactant to drop to one-half of initial value
- $t_{1/2}$ of first order independent of initial concentrations
- half-life same at any given time of reaction
- in first order reaction – concentrations of reactant decreases by ½ in each series of regularly spaced time intervals

14.3.3 Second-Order Reactions

- rate depends on reactant concentration raised to second power or concentrations of two different reactants each raised to first power

$$\text{Rate} = k[A]^2$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$half\ life = t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

- half life dependent on initial concentration of reactant

14.5: Temperature and Rate

- rate constant must increase with increasing temperature, thus increasing the rate of reaction

14.5.1 The Collision Model

- **collision model** – molecules must collide to react
- greater frequency of collisions the greater the reaction rate
- for most reactions only a small fraction of collisions leads to a reaction

14.5.2 Activation Energy

- Svante August Arrhenius
- Molecules must have a minimum amount of energy to react
- Energy comes from kinetic energy of collisions
- Kinetic energy used to break bonds
- Activation energy, E_a – minimum energy required to initiate a chemical reaction
- Activated complex or transition state – atoms at the top of the energy barrier
- Rate depends on temperature and E_a
- Lower E_a means faster reaction
- Reactions occur when collisions between molecules occur with enough energy and proper orientation

14.5.3 The Arrhenius Equation

- reaction rate data:
- theArrhenius Equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

- k = rate constant, E_a = activation energy, R = gas constant (8.314 J/(mol K)), T = absolute temperature, A = frequency factor
- A relates to frequency of collisions, favorable orientations

$$\ln k = -\frac{E_a}{RT} + \ln A$$

- the $\ln k$ vs. $1/t$ graph (also known as an Arrhenius plot) has a slope $-E_a/R$ and the y-intercept $\ln A$
- for two temperatures:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- used to calculate rate constant, k_1 and T_1

14.6: Reaction Mechanisms

- **reaction mechanism** – process by which a reaction occurs

14.6.1 Elementary Steps

- **elementary steps** – each step in a reaction
- **molecularity** – if only one molecule involved in step
- **unimolecular** – if only one molecule involved in step
- **bimolecular** – elementary step involving collision of two reactant molecules
- **termolecular** – elementary step involving simultaneous collision of three molecules
- elementary steps in multi-step mechanism must always add to give chemical equation of overall process
- **intermediate** – product formed in one step and consumed in a later step

14.6.2 Rate Laws of Elementary Steps

- if reaction is known to be an elementary step then the rate law is known
- rate of unimolecular step is first order (Rate = k[A])
- rate of bimolecular steps is second order (Rate = k[A][B])
- first order in [A] and [B]
- if double [A] than number of collisions of A and B will double

14.6.3 Rate Laws of Multi-step Mechanisms

- **rate-determining step** – slowest elementary step
- determines rate law of overall reaction

14.6.4 Mechanisms with an Initial Slow Step vs. Mechanisms with an Initial Fast Step

- intermediates are usually unstable, in low concentration, and difficult to isolate
- when a fast step precedes a slow one, solve for concentration of intermediate by assuming that equilibrium is established in fast step

14.7: Catalysis

- **catalyst** – substance that changes speed of chemical reaction without undergoing a permanent chemical change

14.7.1 Homogeneous Catalysis

- **homogeneous catalyst** – catalyst that is present in same phase as reacting molecule
- catalysts alter E_a or A
- generally catalysts lowers overall E_a for chemical reaction
- catalysts provides a different mechanism for reaction

14.7.2 Heterogeneous Catalysis

- exists in different phase from reactants
- initial step in heterogeneous catalyst is adsorption
- **adsorption** – binding of molecules to surface
- adsorption occurs because ions/atoms at surface of solid extremely reactive

14.7.3 Enzymes

- biological catalysts
- large protein molecules with molecular weights 10,000 – 1 million amu
- **catalase** – enzyme in blood and liver that decomposes hydrogen peroxide into water and oxygen
- **substrates** – substances that undergo reaction at the active site
- **lock-and-key model** – substrate molecules bind specifically to the active site
- **enzyme-substrate complex** – combination of enzyme and substrate
- binding between enzyme and substrate involves intermolecular forces (dipole-dipole, hydrogen bonding, and London dispersion forces)
- product from reaction leaves enzyme allowing for another substrate to enter enzyme
- **enzyme inhibitors** – molecules that bind strongly to enzymes
- **turnover number** – number of catalyzed reactions occurring at a particular active site
- large turnover numbers = low activation energies

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15: CHEMICAL EQUILIBRIUM

We introduced the concept of equilibrium in Chapter 11, where you learned that a liquid and a vapor are in equilibrium when the number of molecules evaporating from the surface of the liquid per unit time is the same as the number of molecules condensing from the vapor phase. Vapor pressure is an example of a *physical equilibrium* because only the physical form of the substance changes. Similarly, in Chapter 13, we discussed saturated solutions, another example of a physical equilibrium, in which the rate of dissolution of a solute is the same as the rate at which it crystallizes from solution.

In this chapter, we describe the methods chemists use to quantitatively describe the composition of chemical systems at equilibrium, and we discuss how factors such as temperature and pressure influence the equilibrium composition. As you study these concepts, you will also learn how urban smog forms and how reaction conditions can be altered to produce H_2 rather than the combustion products CO_2 and H_2O from the methane in natural gas. You will discover how to control the composition of the gases emitted in automobile exhaust and how synthetic polymers such as the polyacrylonitrile used in sweaters and carpets are produced on an industrial scale.

15.1: The Concept of Equilibrium

15.2: The Equilibrium Constant

15.3: Interpreting and Working with Equilibrium Constants

15.4: Heterogeneous Equilibria

15.5: Calculating Equilibrium Constants

15.6: Applications of Equilibrium Constants

15.7: Le Chatelier's Principle

15.E: Exercises

15.S: Chemical Equilibrium (Summary)

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15.1: The Concept of Equilibrium

Learning Objectives

- To understand what is meant by chemical equilibrium.

In the last chapter, we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.



Figure 15.1.1: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at –196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. (CC BY-SA 3.0; Eframgoldberg).

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide ($\mathrm{N_2O_4}$) to nitrogen dioxide ($\mathrm{NO_2}$). You may recall that $\mathrm{NO_2}$ is responsible for the brown color we associate with smog. When a sealed tube containing solid $\mathrm{N_2O_4}$ (mp = –9.3°C; bp = 21.2°C) is heated from –78.4°C to 25°C, the red-brown color of $\mathrm{NO_2}$ appears (Figure 15.1.1). The reaction can be followed visually because the product ($\mathrm{NO_2}$) is colored, whereas the reactant ($\mathrm{N_2O_4}$) is colorless:

$$\underset{colorless}{\mathrm{N_2O_4\,(g)}} \underset{\mathrm{k_r}}{\overset{\mathrm{k_f}}{\rightleftharpoons}} \underset{red-brown}{\mathrm{2\,NO_2\,(g)}} \tag{15.1.1}$$

The double arrow indicates that both the forward reaction

$$\mathrm{N_2O_4\,(g)} \xrightarrow{\mathrm{k_f}} \mathrm{2\,NO_2\,(g)} \tag{15.1.2}$$

and reverse reaction

$$\mathrm{2\,NO_2\,(g)} \xrightarrow{\mathrm{k_r}} \mathrm{N_2O_4\,(g)} \tag{15.1.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium as the following chapter demonstrates.

Figure 15.1.2 shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO_2 were zero, then it increases as the concentration of N_2O_4 decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N_2O_4 but an initial NO_2 concentration twice the initial concentration of N_2O_4 (Figure 15.1.2*a*), in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 15.1.2*b*). Thus equilibrium can be approached from either direction in a chemical reaction.

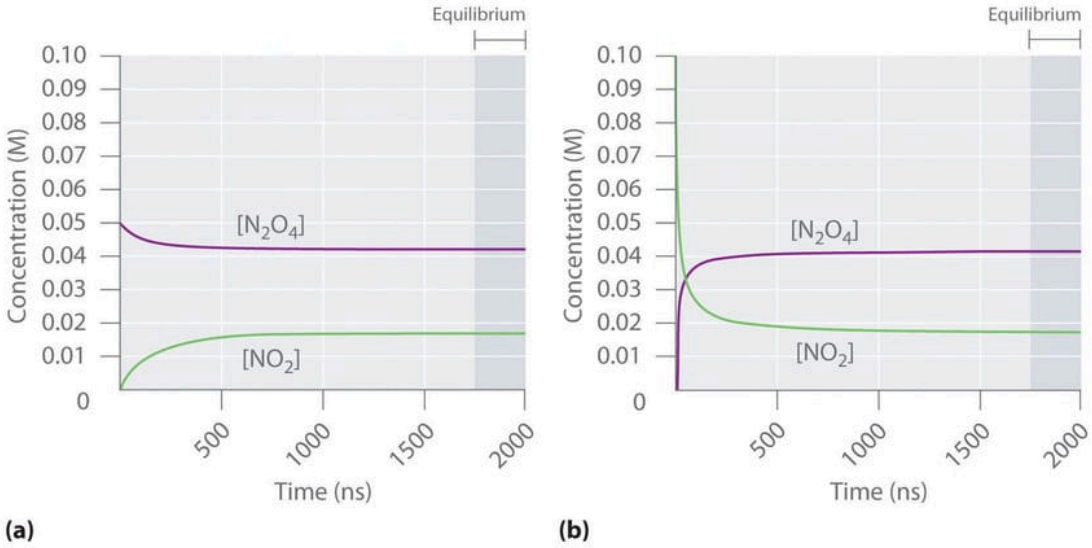


Figure 15.1.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: [N_2O_4] = 0.0422 M and [NO_2] = 0.0156 M at equilibrium. (CC BY-SA-NC; Anonymous by request)

Figure 15.1.3 shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high ($2.0 \times 10^6\ M/s$), but it decreases rapidly as the concentration of NO_2 decreases. As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equations 15.1.1 and 15.1.2). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.

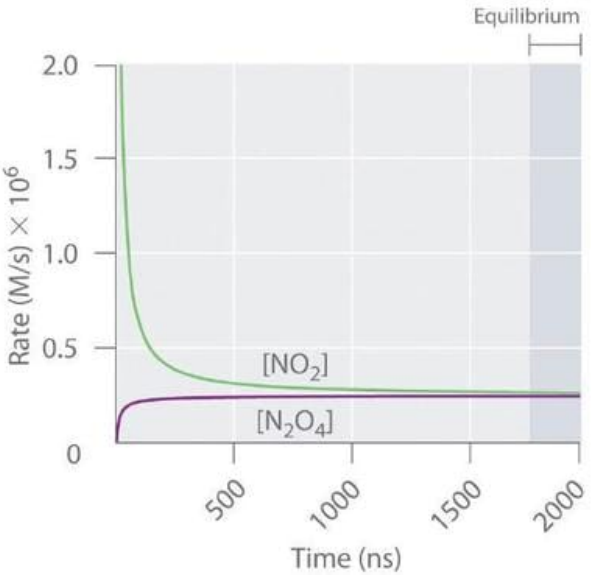


Figure 15.1.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \diamondsuit 2NO_{2(g)}$ System Shown in Part (b) in Figure 15.1.2. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of $\mathrm{NO_2}$ (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of $\mathrm{N_2O_4}$ is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the $\mathrm{N_2O_4}$ concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of $\mathrm{N_2O_4}$ and $\mathrm{NO_2}$ no longer change.

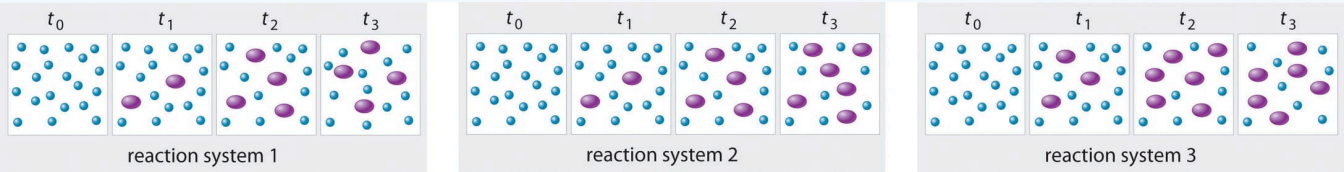
At equilibrium, the forward reaction rate is equal to the reverse reaction rate.

Example 15.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B$$

where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



In reaction system 1 theree are four purple ovals at t3. In reaction system 2 there are size purple ovals at t3. In reaction system systems there are six ovals at t2 and t3.

Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

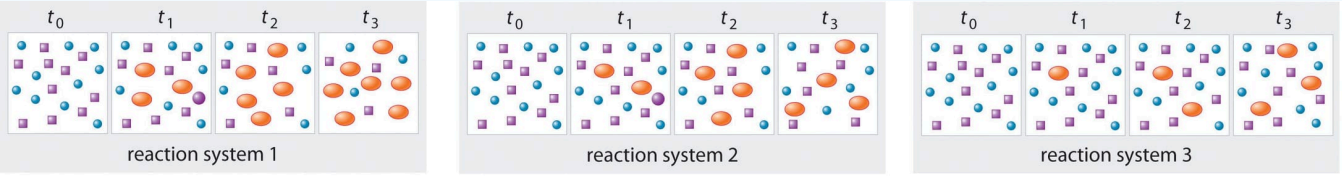
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise 15.1.1

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



In reaction system 1 there are seven orange ovals at t3. In reaction system two there are four orange ovals at t3. In reaction system three there are three orange ovals at t3.

Answer available at the end of this section.

YouTube Video

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A Video Introduction to Dynamic Equilibrium: Introduction to Dynamic Equilibrium(opens in new window) [youtu.be]

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

Answers

Exercise 15.1.1

system 2

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15.2: The Equilibrium Constant

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of $\mathrm{N_2O_4}$ to $\mathrm{NO_2}$. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[\mathrm{N_2O_4}]$$

and

$$\text{reverse rate} = k_r[\mathrm{NO_2}^2]$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[\mathrm{N_2O_4}] = k_r[\mathrm{NO_2}^2] \tag{15.2.1}$$

so

$$\frac{k_f}{k_r} = \frac{[\mathrm{NO_2}^2]}{[\mathrm{N_2O_4}]} \tag{15.2.2}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{15.2.3}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

> The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.

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A Video for Determining the Equilibrium Expression: Determining the Equilibrium Expression(opens in new window) [youtu.be]

Table 15.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 15.2.1. At equilibrium the magnitude of the quantity $[\mathrm{NO_2}^2]/[\mathrm{N_2O_4}]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ are, at equilibrium the quantity $[\mathrm{NO_2}^2]/[\mathrm{N_2O_4}]$ will always be $6.53 \pm 0.03 \times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions. That is, at a

given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 15.2.1: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2^2]/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{15.2.4}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action (or law of chemical equilibrium) and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.2.5}$$

where K is the equilibrium constant for the reaction. Equation 15.2.4 is called the equilibrium equation, and the right side of Equation 15.2.5 is called the equilibrium constant expression. The relationship shown in Equation 15.2.5 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 15.2.2, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

*Table 15.2.2: Equilibrium Constants for Selected Reactions**

Reaction	Temperature (K)	Equilibrium Constant (K)
$S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$	300	4.4×10^{53}
$2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H2O_{(g)}$	500	2.4×10^{47}
$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$	300	1.6×10^{33}
$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$	300	4.1×10^{18}
$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$	300	4.2×10^{13}
***Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.**		

Reaction	Temperature (K)	Equilibrium Constant (K)
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	300	2.7×10^{8}
$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$	100	1.92
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	300	2.9×10^{-1}
$I_{2(g)} \rightleftharpoons 2I_{(g)}$	800	4.6×10^{-7}
$Br_{2(g)} \rightleftharpoons 2Br_{(g)}$	1000	4.0×10^{-7}
$Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$	1000	1.8×10^{-9}
$F_{2(g)} \rightleftharpoons 2F_{(g)}$	500	7.4×10^{-13}
***Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.**		

Effective vs. True Concentrations

You will also notice in Table 15.2.2 that equilibrium constants have no units, even though Equation 15.2.5 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 15.2.6, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{15.2.6}$$

Because equilibrium constants are calculated using "effective concentrations" relative to a standard state of 1 M, values of K are unitless.

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$\mathrm{H_2\,(g) + D_2\,(g) \rightleftharpoons 2\,HD\,(g)}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 15.2.3 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants $\rightleftharpoons$ products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 15.2.6 and 15.2.5), when $k_f \gg k_r$, K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

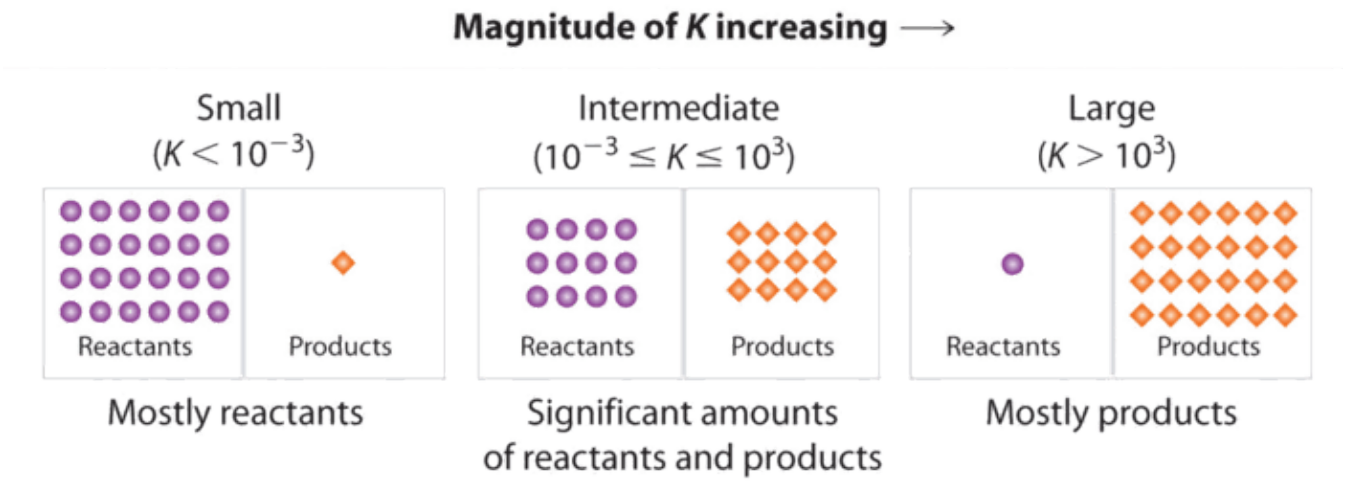


Figure 15.2.3: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

If K is less than 0.001, it is considered small and it will be mostly reactants. If K is greater than 1000, it is considered large and it will be mostly products. If K is greater than or equal to 0.001 and less than or equal to 1000, it is considered intermediate. there will be significant amounts or reactants and products.

A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

Example 15.2.1: Equilibrium Constant Expressions

Write the equilibrium constant expression for each reaction.

- $\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$
- $\mathrm{CO\,(g) + \frac{1}{2}\,O_2\,(g) \rightleftharpoons CO_2\,(g)}$
- $\mathrm{2\,CO_2\,(g) \rightleftharpoons 2\,CO\,(g) + O_2\,(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 15.2.5. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, $\mathrm{N_2}$ has a coefficient of 1 and $\mathrm{H_2}$ has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[\mathrm{NH_3}^2]}{[\mathrm{N_2}][\mathrm{H_2}]^3}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and $\mathrm{O_2}$, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2{}^{1/2}]}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2

$$\frac{[CO]^2[O_2]}{[CO_2{}^2]}$$

Exercise 15.2.1

Write the equilibrium constant expression for each reaction.

a. $N_2O\,(g) \rightleftharpoons N_2\,(g) + \frac{1}{2}\,O_2\,(g)$
b. $2\,C_8H_{18}\,(g) + 25\,O_2\,(g) \rightleftharpoons 16\,CO_2\,(g) + 18\,H_2O\,(g)$
c. $H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$

Answer a available at the end of this section.

Example 15.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 15.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3\,H_2\,(g) + N_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25°C} = 3.3 \times 10^8$,
- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a available at the end of this section.

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Video which Discusses What Does K Tell us About a Reaction?: What Does K Tell us About a Reaction?(opens in new window) [youtu.be]

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 15.2.4 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{15.2.7}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{15.2.8}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $\mathrm{N_2O_4} \rightleftharpoons 2\,\mathrm{NO_2}$ is as follows:

$$K = \frac{[\mathrm{NO_2}^2]}{[\mathrm{N_2O_4}]} \tag{15.2.9}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}^2]} \tag{15.2.10}$$

Consider another example, the formation of water:

$$2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{H_2O\,(g)}.$$

Because $\mathrm{H_2}$ is a good reductant and $\mathrm{O_2}$ is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form $\mathrm{O_2}$ and $\mathrm{H_2}$, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into $\mathrm{H_2}$ and $\mathrm{O_2}$.

The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as

written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2\,NO_2 \rightleftharpoons N_2O_4$$

as

$$NO_2 \rightleftharpoons \tfrac{1}{2}\,N_2O_4$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4{}^{1/2}]}{[NO_2]} \tag{15.2.11}$$

The values for K′ (Equation 15.2.10) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{15.2.12}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the nth power.

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A Video Discussing Relationships Involving Equilibrium Constants: Relationships Involving Equilibrium Constants(opens in new window) [youtu.be] (opens in new window)

Example 15.2.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

What is the equilibrium constant for each related reaction at 745 K?

a. $2\,NH_3\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2\,(g)$
b. $\tfrac{1}{2}\,N_2\,(g) + \tfrac{3}{2}\,H_2\,(g) \rightleftharpoons NH_3\,(g)$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $N_{2(g)}$ with $H_{2(g)}$ to produce $NH_{3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

Exercise

At 527°C, the equilibrium constant for the reaction

$$2\,\mathrm{SO_2\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{SO_3\,(g)}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$\mathrm{SO_3\,(g)} \rightleftharpoons \mathrm{SO_2\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)}$$

Answer available at the end of this section.

Equilibrium Constant Expressions for Systems that Contain Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction $aA + bB \rightleftharpoons cC + dD$, in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{15.2.13}$$

Thus K_p for the decomposition of N_2O_4 (Equation 15.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{15.2.14}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an “effective pressure,” the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The “effective pressure” is called the fugacity, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the absolute temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{15.2.15}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of **gaseous** products and **gaseous** reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 15.2.15, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$

). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

\[K_p = K(RT)^1 = KRT \nonumber \]

Example 15.2.4: The Haber Process (again)

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$$

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 15.2.15 to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745$ K. Thus, from Equation 15.2.12, we have the following:

$$\begin{aligned} K_p &= K(RT)^{-2} \\ &= \frac{K}{(RT)^2} \\ &= \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} \\ &= 3.16 \times 10^{-5} \end{aligned}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise 15.2.4

Calculate K_p for the reaction

$$\mathrm{2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer available at the end of this section.

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Video Discussing Converting Kc to Kp: Converting Kc to Kp(opens in new window) [youtu.be]

Equilibrium Constant Expressions for the Sums of Reactions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of $\mathrm{N_2}$ with $\mathrm{O_2}$ to give $\mathrm{NO_2}$. This reaction is an important source of the $\mathrm{NO_2}$ that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (step 1), $\mathrm{N_2}$ reacts with $\mathrm{O_2}$ at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional $\mathrm{O_2}$ to give $\mathrm{NO_2}$ (step 2). The equilibrium constant for each reaction at 100°C is also given.

$$\mathrm{N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)} \qquad K_1 = 2.0 \times 10^{-25}$$

$$\mathrm{2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)} \qquad K_2 = 6.4 \times 10^{9}$$

Summing reactions (step 1) and (step 2) gives the overall reaction of N_2 with O_2:

$$\mathrm{N_2\,(g) + 2\,O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)} \qquad K_3 = ?$$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}\,[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

> To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.

Example 15.2.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \qquad K_2 = 3.3 \times 10^{4}$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3$$

Exercise 15.2.6

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$ $\quad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $\quad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $\quad K_3 = ?$

Answer available at the end of this section.

Summary

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas during the reaction. An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n}$$

Answers

Exercise 15.2.1

$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$

$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$

$K = \frac{[HI]^2}{[H_2][I_2]}$

Exercise 15.2.2

327°C, where K is smallest

25°C

Exercise

3.6×10^{-3}

Exercise 15.2.4

$K_p = 1.2 \times 10^3$

Exercise 15.2.6

$K_3 = 1.1 \times 10^{66}$

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15.3: Interpreting and Working with Equilibrium Constants

Learning Objectives

- How to figure out in which direction a reaction will go (i.e. towards making product, or more reactant)
- Calculating equilibrium concentrations. This may involve knowing equilibrium values for some of the reactants and products and determining the concentration of an unknown.
- Alternatively, we may be provided with the starting concentrations of reactants and products and may be asked to find the equilibrium concentrations

Your ability to interpret the numerical value of a quantity in terms of what it means in a practical sense is an essential part of developing a working understanding of Chemistry. This is particularly the case for equilibrium constants, whose values span the entire range of the positive numbers. Although there is no explicit rule, for most practical purposes you can say that equilibrium constants within the range of roughly 0.01 to 100 indicate that a chemically significant amount of all components of the reaction system will be present in an equilibrium mixture and that the reaction will be ***incomplete*** or "***reversible***".

As an equilibrium constant approaches the limits of zero or infinity, the reaction can be increasingly characterized as a one-way process; we say it is "***complete***" or "***irreversible***". The latter term must of course not be taken literally; the Le Chatelier principle still applies (especially insofar as temperature is concerned), but addition or removal of reactants or products will have less effect.

Kinetically Hindered Reactions

Although it is by no means a general rule, it frequently happens that reactions having very large equilibrium constants are kinetically hindered, often to the extent that the reaction essentially does not take place.

The examples in the following table are intended to show that numbers (values of *K*), no matter how dull they may look, do have practical consequences!

Table 15.3.1*: Examples of Reversible Reactions*

Reaction	K	remarks
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$	5×10^{-31} at 25°C, 0.0013 at 2100°C	These two very different values of *K* illustrate very nicely why reducing combustion-chamber temperatures in automobile engines is environmentally friendly.
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	7×10^{5} at 25°C, 56 at 1300°C	See the discussion of this reaction in the section on the Haber process.
$H_{2(g)} \rightleftharpoons 2H_{(g)}$	10^{-36} at 25°C, 6×10^{-5} at 5000°	Dissociation of any stable molecule into its atoms is endothermic. This means that all molecules will decompose at sufficiently high temperatures.

$H_2O_{(g)} \rightleftharpoons H_{2(g)} + ½O_{2(g)}$	8×10^{-41} at 25°C	You won't find water a very good source of oxygen gas at ordinary temperatures!
$CH_3COOH_{(l)} \rightleftharpoons 2H_2O_{(l)} + 2C_{(s)}$	$K_c = 10^{13}$ at 25°C	This tells us that acetic acid has a great tendency to decompose to carbon, but nobody has ever found graphite (or diamonds!) forming in a bottle of vinegar. A good example of a super kinetically-hindered reaction!

Do Equilibrium Constants have Units?

The equilibrium expression for the synthesis of ammonia

$$3\,\mathrm{H_2\,(g)} + \mathrm{N_2\,(g)} \longrightarrow 2\,\mathrm{NH_3\,(g)} \tag{15.3.1}$$

can be expressed as

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} \tag{15.3.2}$$

or

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \tag{15.3.3}$$

so K_p for this process would appear to have units of atm^{-2}, and K_c would be expressed in mol^{-2} L^2. And yet these quantities are often represented as being dimensionless. Which is correct? The answer is that both forms are acceptable. There are some situations (which you will encounter later) in which *K*'s must be considered dimensionless, but in simply quoting the value of an equilibrium constant it is permissible to include the units, and this may even be useful in order to remove any doubt about the units of the individual terms in equilibrium expressions containing both pressure and concentration terms. In carrying out your own calculations, however, there is rarely any real need to show the units.

Strictly speaking, equilibrium expressions do not have units because the concentration or pressure terms that go into them are really *ratios* having the forms (*n* mol L^{-1})/(1 mol L^{-1}) or (*n* atm)/(1 atm) in which the unit quantity in the denominator refers to the *standard state* of the substance; thus the units always cancel out.

> Strictly speaking, equilibrium expressions do not have units.

For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid, so for something like $\mathrm{CaF\,(s)}$, the term going into the equilibrium expression is $[\mathrm{CaF_2}]/[\mathrm{CaF_2}]$ which cancels to unity; this is the reason we do not need to include terms for solid or liquid phases in equilibrium expressions. The subject of standard states would take us beyond where we need to be at this point in the course, so we will simply say that the concept is made necessary by the fact that energy, which ultimately governs chemical change, is always relative to some arbitrarily defined zero value which, for chemical substances, is the standard state.

Summary

The magnitude of the equilibrium constant, K, indicates the extent to which a reaction will proceed:

- If K is a large number, it means that the equilibrium concentration of the products is large. In this case, the reaction as written will proceed to the right (resulting in an increase in the concentration of products)
- If K is a small number, it means that the equilibrium concentration of the reactants is large. In this case, the reaction as written will proceed to the left (resulting in an increase in the concentration of reactants)

Knowing the value of the equilibrium constant, K, will allow us to determine: (1) he direction a reaction will proceed to achieve equilibrium and (2) the ratios of the concentrations of reactants and products when equilibrium is reached

Contributors and Attributions

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15.4: Heterogeneous Equilibria

Learning Objectives

- To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as CaF_2(s), the term going into the equilibrium expression is [CaF_2]/[CaF_2] which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2\,(g) + C\,(s)} \rightleftharpoons \mathrm{2\,CO\,(g)} \tag{15.4.1}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

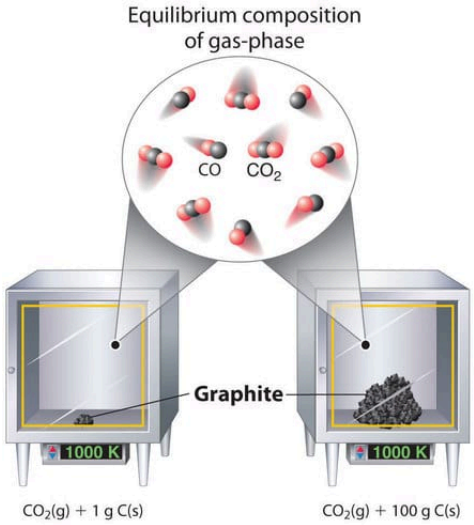
$$K = \frac{a_{\mathrm{CO}}^2}{a_{\mathrm{CO_2}} a_C} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}][1]} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}]} \tag{15.4.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{15.4.3}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and $\mathrm{CO_2}$, the system described in Equation 15.4.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 15.4.1, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.



$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Figure 15.4.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 15.4.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $\mathrm{PCl_3\,(l) + Cl_2\,(g) \rightleftharpoons PCl_5\,(s)}$
b. $\mathrm{Fe_3O_4\,(s) + 4\,H_2\,(g) \rightleftharpoons 3\,Fe\,(s) + 4\,H_2O\,(g)}$

Given: balanced equilibrium equations.

Asked for: expressions for K and K_p.

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[Cl_2]}$$

and

$$K_p = \frac{1}{(1)P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:

$$K = \frac{(1)[H_2O]^4}{(1)[H_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

Exercise 15.4.1

Write the expressions for K and K_p for the following reactions.

a. $\mathrm{CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)}$
b. $\underset{glucose}{\mathrm{C_6H_{12}O_6\,(s)}} + \mathrm{6\,O_2\,(g) \rightleftharpoons 6\,CO_2\,(g) + 6\,H_2O\,(g)}$

Answer a available at the end of this section.

For reactions carried out in solution, the solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms.* The activities of the solutes are approximated by their molarities.

Summary

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

Contributors and Attributions

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Answers

Exercise 15.4.1

$K = [\mathrm{CO_2}]$ and $K_p = P_{\mathrm{CO_2}}$

$K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

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15.5: Calculating Equilibrium Constants

Learning Objectives

- To solve quantitative problems involving chemical equilibriums.

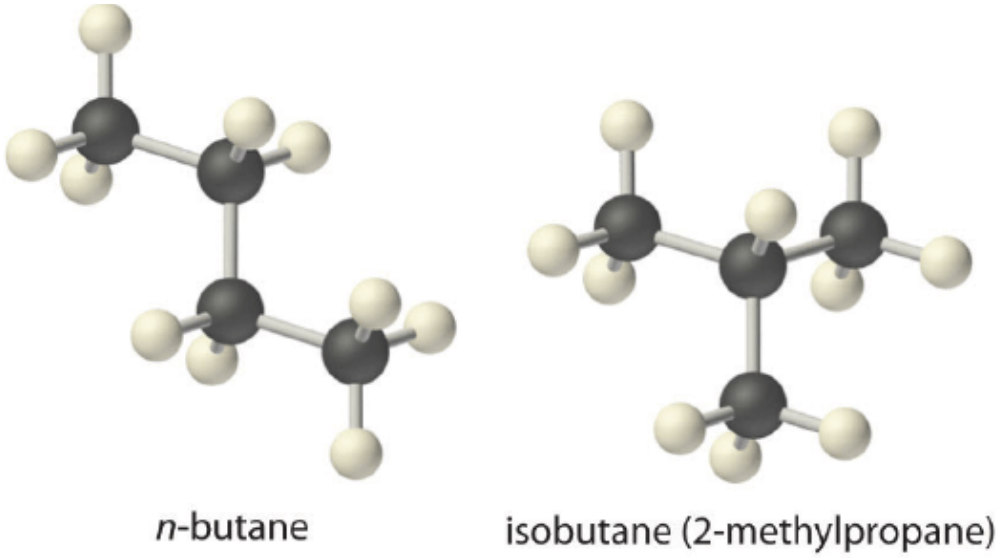
There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

We saw in the exercise in Example 6 in Section 15.2 that the equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3}. (Remember that equilibrium constants are unitless.)

A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



This reaction can be written as follows:

$$n\text{-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{15.5.1}$$

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{[isobutane]}{[n\text{-}butane]} = 0.041\ M = 2.6 \tag{15.5.2}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 15.5.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ SO_3$,
- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we use the relationship derived previously

$$K_p = K(RT)^{\Delta n}$$

where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4[(0.08206\ L \cdot atm/mol \cdot K)(800K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

Exercise 15.5.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$2NOCl_{(g)} \leftrightharpoons 2NO_{(g)} + Cl_{2(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K and K_p for this reaction.

Answer available at the end of this section.

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example $15.5.2$ shows one way to do this.

Example 15.5.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

\[2 NOCl_{(g)} \rightleftharpoons 2NO_{(g)}+Cl_{2(g)}\nonumber \]

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).
B. Calculate all possible initial concentrations from the data given and insert them in the table.
C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.
D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$. The initial concentrations of NO and Cl_2 are $0\ M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$. We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	\([NOCl]	$[NO]$	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

Exercise 15.5.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ \ M\ \ H_2$ and $0.0416\ \ M\ \ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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A Video Disucssing Using ICE Tables to find Kc: Using ICE Tables to find Kc(opens in new window) [youtu.be]

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 15.5.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 15.5.2.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as $+x$, then the change in the concentration of n-butane is Δ[n-butane] = $-x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	[n-butane$_{(g)}$]	[isobutane$_{(g)}$]
Initial	1.00	0
Change	$-x$	$+x$
Final	$(1.00 - x)$	$(0 + x) = x$

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6$$

Rearranging and solving for x,

$$x = 2.6(1.00 - x) = 2.6 - 2.6x$$

$$x + 2.6x = 2.6$$

$$x = 0.72$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6$$

This is the same K we were given, so we can be confident of our results.

Example 15.5.3 illustrates a common type of equilibrium problem that you are likely to encounter.

Example 15.5.3: The water–gas shift reaction

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K, and initial concentrations

Asked for: final concentrations

Strategy:

A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.
B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial	0.0150	0.0150	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.0150 - x)$	$(0.0150 - x)$	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150 - x)(0.0150 - x} = \frac{x^2}{(0.0150 - x)^2} = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150 - x)^2} = \left(\frac{x}{0.0150 - x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x}{(0.0150 - x)} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

Exercise 15.5.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$K = 54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer available at the end of this section.

In Example 15.5.3, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example 15.5.4.

Example 15.5.4

In the water–gas shift reaction shown in Example 15.5.3, a sample containing 0.632 M CO2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (\(x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632 \ \ M$ and $[H_2]_i = 0.570 \ \ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.570 - x)$	$(0.632 - x)$	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 15.5.3, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.202x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, and $\Delta[H_2] = \Delta[CO_2] = -0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f[= [H_2]_i + \Delta[H_2] = 0.570\ M - 0.148\ M = 0.422M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = 0.632\ M - 0.148\ M = 0.484M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = 0\ M + 0.148\ M = 0.148\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = 0M + 0.148\ M = 0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

Exercise 15.5.4

The exercise in Example 15.5.1 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer available at the end of this section.

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \leq 10^{-3}$) or very large ($K \geq 10^3$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 15.5.5.

Example 15.5.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

with $K_p = 2.0 \times 10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm, $P_{N_2} = 0.78\ atm$ and $P_{O_2} = 0.21\ atm$?

Given: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (\(x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in the partial pressure of O_2 and of N_2 is $-x$ because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	$-x$	$-x$	$+2x$
Final	$(0.78 - x)$	$(0.21 - x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, $(0.78 - x) = 0.78$ and $(0.21 - x) = 0.21$. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x = 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x \ \ atm = 1.8 \times 10^{-16} \ \ atm$
- $P_{N_2} = (0.78 - x) \ \ atm = 0.78 \ \ atm$
- $P_{O_2} = (0.21 - x) \ \ atm = 0.21 \ \ atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^{3}$, then the assumption is justified. Otherwise, we must use the quadratic formula

or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

Exercise 15.5.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21\ atm$)?

Answer available at the end of this section.

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^3$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example 15.5.6.

Example 15.5.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A. Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.
B. Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).
C. Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 15.5.5. If we

define $-x$ as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is $+x$. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[H_{2(g)}]$	$[C_2H_{4(g)}]$	$[C_2H_{6(g)}]$
Initial	0.200	0.155	0
Assuming 100% reaction	0.045	0	0.155
Change	$+x$	$+x$	$-x$
Final	$(0.045 + x)$	$(0 + x)$	$(0.155 - x)$

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified ($(0.045 + x)$ = 0.045 and $(0.155 - x) = 0.155$) as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ \ M = 0.155\ \ M$
- $[C_2H_4]_f = x\ \ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ \ M = 0.045\ \ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

Exercise 15.5.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer available at the end of this section.

YouTube Video

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A Video Discussing Using ICE Tables to find Eq. Concentrations & Kc: Using ICE Tables to find Eq. Concentrations & Kc(opens in new window) [youtu.be]

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture. When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

Answers

Exercise 15.5.1

$K = 48.8$ and $K_p = 48.8$

Exercise 15.5.2

$K = 0.105$ and $K_p = 2.61 \times 10^{-5}$

Exercise 15.5.3

- $[HI]_f = 0.270\ M$
- $[H_2]_f = [I_2]_f = 0.037\ M$

Exercise 15.5.4

- $[H_I]_f = 0.0882\ M$
- $[H_2]_f = 0.156\ M$
- $[I_2]_f = 9.2 \times 10^{-4} M$

Exercise 15.5.5

$4.8 \times 10^{-31}\ atm$

Exercise 15.5.6

$[H_2]_f = 4.8 \times 10^{-32}\ M\ [Cl_2]_f = 0.135\ M\ [HCl]_f = 0.514\ M$

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15.6: Applications of Equilibrium Constants

Learning Objectives

- To predict in which direction a reaction will proceed.

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a Quantity called the reaction Quotient (Q). The expression for the reaction Quotient has precisely the same form as the equilibrium constant expression, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the reaction quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.6.1}$$

To understand how information is obtained using a reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons 2\,\mathrm{NO_2\,(g)}$$

for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[\mathrm{NO_2}^2]}{[\mathrm{N_2O_4}]} \tag{15.6.2}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Table 15.6.1*: Equilibrium Experiment data*

Experiment	$[\mathrm{NO_2}]$ (M)	$[\mathrm{N_2O_4}]$ (M)	$Q = \frac{[\mathrm{NO_2}^2]}{[\mathrm{N_2O_4}]}$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is

not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K:

- If $Q = K$, for example, then the system is already at equilibrium, and **no further change** in the composition of the system will occur unless the conditions are changed.
- If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the **right** as written, forming products at the expense of reactants.
- If $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so the reaction will proceed to the **left** as written, forming reactants at the expense of products.

These points are illustrated graphically in Figure 15.6.1.

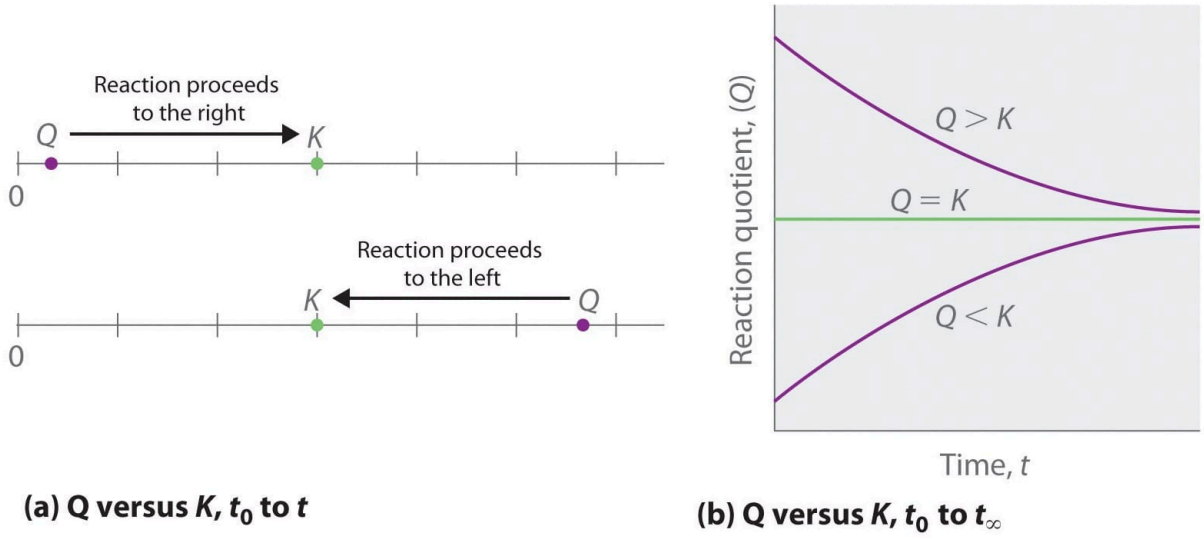


Figure 15.6.1: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.
One way is used two number lines. The second way is to use a graph of reaction quotient against time.

If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.

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A Video Discussing Using the Reaction Quotient (Q): Using the Reaction Quotient (Q) (opens in new window) [youtu.be]

Example 15.6.1

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:

$$\mathrm{CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3\,H_2\,(g)}$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0 × 10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and $\mathrm{H_2}$ or to the left to form $\mathrm{CH_4}$ and $\mathrm{H_2O}$?

Given: balanced chemical equation, K, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A. Calculate the molar concentrations of the reactants and the products.
B. Use Equation 15.6.1 to determine Q. Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A We must first find the initial concentrations of the substances present. For example, we have $1.2 \times 10^{-2} mol$ of $\mathrm{CH_4}$ in a 2.0 L container, so

$$[\mathrm{CH_4}] = \frac{1.2 \times 10^{-2}\,\mathrm{mol}}{2.0\,\mathrm{L}} = 6.0 \times 10^{-3} M$$

We can calculate the other concentrations in a similar way:

- $[\mathrm{H_2O}] = 4.0 \times 10^{-3} M$,
- $[\mathrm{CO}] = 8.0 \times 10^{-3} M$, and
- $[\mathrm{H_2}] = 3.0 \times 10^{-3} M$.

B We now compute Q and compare it with K:

$$\begin{aligned} Q &= \frac{[\mathrm{CO}][\mathrm{H_2}]^3}{[\mathrm{CH_4}][\mathrm{H_2O}]} \\ &= \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} \\ &= 9.0 \times 10^{-6} \end{aligned}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming $\mathrm{H_2}$ and CO at the expense of $\mathrm{H_2O}$ and $\mathrm{CH_4}$.

Exercise 15.6.2

In the water–gas shift reaction introduced in Example 15.6.1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$\mathrm{CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)}$$

$K = 0.64$ at 900 K. If 0.010 mol of both CO and $\mathrm{H_2O}$, 0.0080 mol of $\mathrm{CO_2}$, and 0.012 mol of $\mathrm{H_2}$ are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer available at the end of this section.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Reaction 1

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$\mathrm{PbCO_3\,(s) \rightleftharpoons PbO\,(s) + CO_2\,(g)} \tag{15.6.3}$$

Because $\mathrm{PbCO_3}$ and PbO are solids, the equilibrium constant is simply

$$K = [\mathrm{CO_2}].$$

At a given temperature, therefore, any system that contains solid $\mathrm{PbCO_3}$ and solid PbO will have exactly the same concentration of $\mathrm{CO_2}$ at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure $15.6.3$, which shows a plot of $[\mathrm{CO_2}]$ versus the amount of $\mathrm{PbCO_3}$ added. Initially, the added $\mathrm{PbCO_3}$ decomposes completely to $\mathrm{CO_2}$ because the amount of $\mathrm{PbCO_3}$ is not sufficient to give a $\mathrm{CO_2}$ concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only $\mathrm{CO_2\,(g)}$ and $\mathrm{PbO\,(s)}$. In contrast, when just enough $\mathrm{PbCO_3}$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $\mathrm{PbCO_3}$ has no effect on the $\mathrm{CO_2}$ concentration: the graph is a horizontal line.

Thus any $\mathrm{CO_2}$ concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $\mathrm{PbCO_3}$ and PbO are present. For example, the point labeled **A** in Figure $15.6.2$ lies above the horizontal line, so it corresponds to a $[\mathrm{CO_2}]$ that is greater than the equilibrium concentration of $\mathrm{CO_2}$ (i.e., $Q > K$). To reach equilibrium, the system must decrease $[\mathrm{CO_2}]$, which it can do only by reacting $\mathrm{CO_2}$ with solid PbO to form solid $\mathrm{PbCO_3}$. Thus the reaction in Equation $15.6.3$ will proceed to the left as written, until $[\mathrm{CO_2}] = K$. Conversely, the point labeled **B** in Figure $15.6.2$ lies below the horizontal line, so it corresponds to a $[\mathrm{CO_2}]$ that is less than the equilibrium concentration of $\mathrm{CO_2}$ (i.e., $Q < K$). To reach equilibrium, the system must increase $[\mathrm{CO_2}]$, which it can do only by decomposing solid $\mathrm{PbCO_3}$ to form $\mathrm{CO_2}$ and solid PbO. The reaction in Equation $15.6.3$ will therefore proceed to the right as written, until $[\mathrm{CO_2}] = K$.

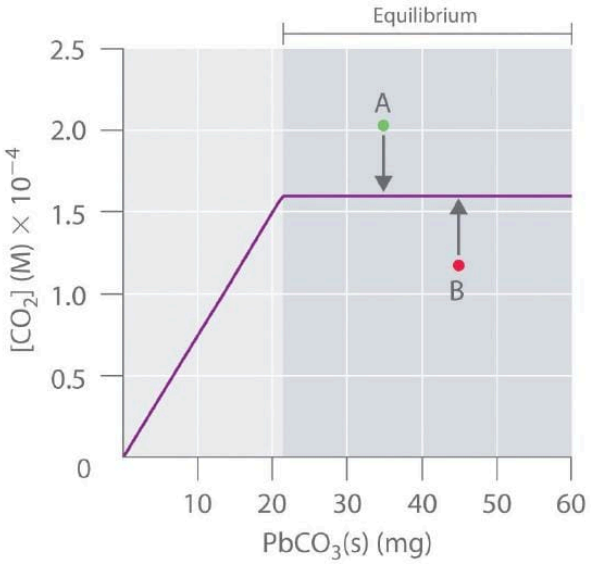


Figure $15.6.2$: The Concentration of Gaseous $\mathrm{CO_2}$ in a Closed System at Equilibrium as a Function of the Amount of Solid $\mathrm{PbCO_3}$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $\mathrm{PbCO_3}$ added, as $\mathrm{PbCO_3}$ decomposes to $\mathrm{CO_2\,(g)}$ and solid PbO . Once the $\mathrm{CO_2}$ concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $\mathrm{PbCO_3}$ has no effect on $[\mathrm{CO_2}]$, as long as the temperature remains constant.

Reaction 2

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$\mathrm{CdO\,(s) + H_2\,(g) \rightleftharpoons Cd\,(s) + H_2O\,(g)} \tag{15.6.4}$$

and the equilibrium constant is

$$K = \frac{[\mathrm{H_2O}]}{[\mathrm{H_2}]}.$$

If $[\mathrm{H_2O}]$ is doubled at equilibrium, then $[\mathrm{H_2}]$ must also be doubled for the system to remain at equilibrium. A plot of $[\mathrm{H_2O}]$ versus $[\mathrm{H_2}]$ at equilibrium is a straight line with a slope of K (Figure 15.6.3). Again, only those pairs of concentrations of $\mathrm{H_2O}$ and $\mathrm{H_2}$ that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 15.6.4 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point **A** in Figure 15.6.3 lies below the line, indicating that the $[\mathrm{H_2O}]/[\mathrm{H_2}]$ ratio is less than the ratio of an equilibrium mixture (i.e., $Q < K$). Thus the reaction in Equation 15.6.4 will proceed to the right as written, consuming $\mathrm{H_2}$ and producing $\mathrm{H_2O}$, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point **B** in Figure 15.6.3 lies above the line, indicating that the $[\mathrm{H_2O}]/[\mathrm{H_2}]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction in Equation 15.6.4 will proceed to the left as written, consuming $\mathrm{H_2O}$ and producing $\mathrm{H_2}$, which causes the concentration ratio to move down and to the right toward the equilibrium line.

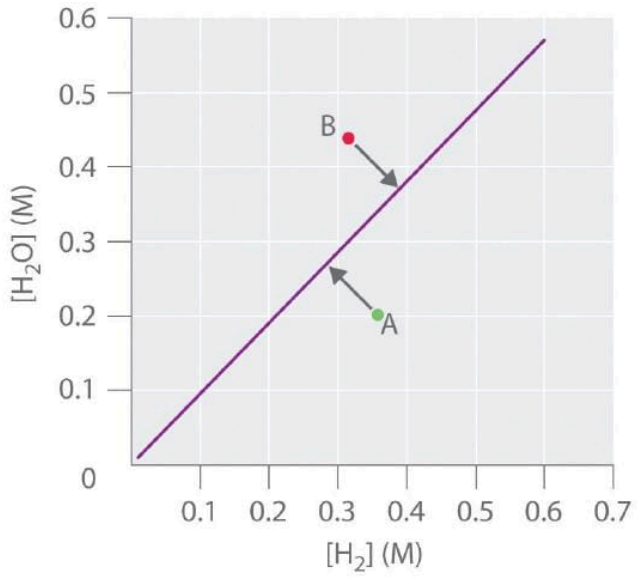


Figure 15.6.3: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of $H_{2(g)}$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.

Reaction 3

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$\mathrm{NH_4I\,(s) \rightleftharpoons NH_3\,(g) + HI\,(g)} \tag{15.6.5}$$

For this system, K is equal to the product of the concentrations of the two products:

$$K = [\mathrm{NH_3}][\mathrm{HI}].$$

If we double the concentration of $\mathrm{NH_3}$, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 15.6.4. As a result, for a given concentration of either HI or $\mathrm{NH_3}$, only a single equilibrium

composition that contains equal concentrations of both $\mathrm{NH_3}$ and HI is possible, for which

$$[\mathrm{NH_3}] = [\mathrm{HI}] = \sqrt{K}.$$

Any point that lies below and to the left of the equilibrium curve (such as point **A** in Figure $15.6.4$) corresponds to $Q < K$, and the reaction in Equation $15.6.5$ will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point **B** in Figure $15.6.5$) corresponds to $Q > K$, and the reaction in Equation $15.6.5$ will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

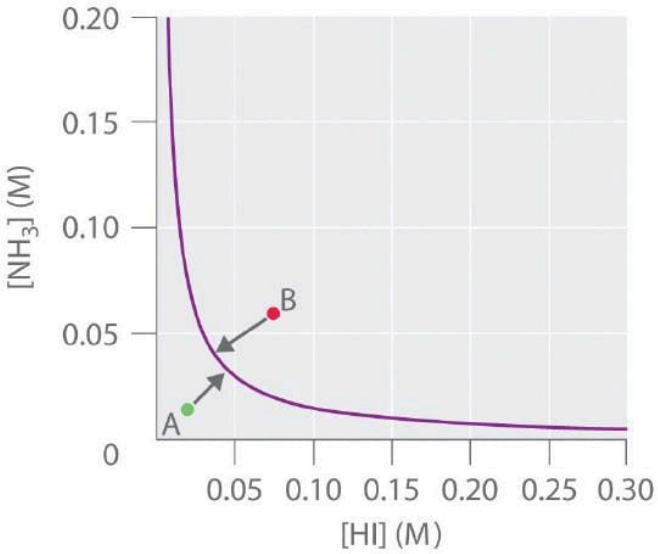


Figure $15.6.4$: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for system in Reaction $15.6.5$ at Equilibrium. Only one equilibrium concentration of $\mathrm{NH_3\,(g)}$ is possible for any given equilibrium concentration of $\mathrm{HI\,(g)}$. In this case, the two are inversely proportional. Thus a large $[\mathrm{HI}]$ at equilibrium requires a small $[\mathrm{NH_3}]$ at equilibrium and vice versa.

Summary

The reaction Quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. The reaction Quotient (Q or Q_p) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

Answers

Exercise $15.6.2$

$Q = 0.96$. Since (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

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15.7: Le Chatelier's Principle

Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if $(Q \leq K)$ or the reactants (if $(Q \geq K)$ until Q returns to the same value as K. This process is described by Le Chatelier's principle.

Le Chatelier's principle

When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Predicting the Direction of a Reversible Reaction

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

> A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in Figure $15.7.1$ is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than *K*). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



Figure 15.7.1: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN– as the white solid AgSCN. $Ag^{+}(aq) + SCN^{-}(aq) \rightleftharpoons AgSCN(s)$. The decrease in the SCN– concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the $Fe(SCN)^{2+}$. (credit: modification of work by Mark Ott).

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \tag{15.7.1}$$

$$K_c = 50.0 \text{ at } 400°C \tag{15.7.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[H_2] = 0.374\ M$,
- $[I_2] = 0.153\ M$, and
- $[HI] = 1.692\ M$.

This gives:

$$\begin{aligned} Q_c &= \frac{[HI]^2}{[H_2][I_2]} \\ &= \frac{(1.692)^2}{(0.374)(0.153)} \\ &= 50.0 = K_c \end{aligned}$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI. **Le Chatelier's Principle (Changing Concentrations):** Le Chatelier's Principle (Changing Concentrations)(opens in new window) [youtu.be]

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A Video Discussing Le Chatelier's Principle (Changing Concentrations): Le Chatelier's Principle (Changing Concentrations)(opens in new window) [youtu.be] (opens in new window)

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, $\mathrm{O_2}$, and $\mathrm{NO_2}$ are at equilibrium:

$$2\,\mathrm{NO\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{NO_2\,(g)} \tag{15.7.3}$$

The formation of additional amounts of $\mathrm{NO_2}$ decreases the total number of molecules in the system because each time two molecules of $\mathrm{NO_2}$ form, a total of three molecules of NO and $\mathrm{O_2}$ are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of $\mathrm{NO_2}$ into NO and $\mathrm{O_2}$, which tends to restore the pressure.

Now consider this reaction:

$$\mathrm{N_2\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{NO\,(g)} \tag{15.7.4}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

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Le Chatelier's Principle (Changes in Pressure or Volume):

Le Chatelier's Principle (Changes in Pressure or Volume)(opens in new window) [youtu.be]

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$\mathrm{H_2\,(g) + I_2\,(g) \;\rightleftharpoons\; 2\,HI\,(g)} \quad \Delta H = -9.4\ \mathrm{kJ\ (exothermic)} \tag{15.7.5}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$\mathrm{H_2\,(g) + I_2\,(g) \;\rightleftharpoons\; 2\,HI\,(g) + heat} \tag{15.7.6}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ in this reaction

$$\mathrm{N_2O_4\,(g) \;\rightleftharpoons\; 2\,NO_2\,(g)} \quad \Delta H = 57.20\ \mathrm{kJ} \tag{15.7.7}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\mathrm{heat + N_2O_4\,(g) \;\rightleftharpoons\; 2\,NO_2\,(g)} \tag{15.7.8}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown $\mathrm{NO_2}$ molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless $\mathrm{N_2O_4}$ increases, and the concentration of brown $\mathrm{NO_2}$ decreases, causing the brown color to fade.

The overview of how different disturbances affect the reaction equilibrium properties is tabulated in Table 15.7.1.

Table 15.7.1: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Example 15.7.1

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

a. $2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + \mathbf{O}_{2(g)}$: the amount of HgO is doubled.
b. $NH_4HS_{(s)} \rightleftharpoons \mathbf{NH}_{3(g)} + H_2S_{(g)}$: the concentration of H_2S is tripled.
c. $\mathbf{n\text{-}butane}_{(g)} \rightleftharpoons isobutane_{(g)}$: the concentration of isobutane is halved.

Given: equilibrium systems and changes

Asked for: equilibrium constant expressions and effects of changes

Strategy:

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

Solution:

Because $HgO_{(s)}$ and $Hg_{(l)}$ are pure substances, they do not appear in the equilibrium constant expression. Thus, for this reaction, $K = [O_2]$. The equilibrium concentration of O_2 is a constant and does not depend on the amount of HgO present. Hence adding more HgO will not affect the equilibrium concentration of O_2, so no compensatory change is necessary.

NH_4HS does not appear in the equilibrium constant expression because it is a solid. Thus $K = [NH_3][H_2S]$, which means that the concentrations of the products are inversely proportional. If adding H_2S triples the H_2S concentration, for example, then the NH_3 concentration must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations equals K.

For this reaction, $K = \frac{[isobutane]}{[n\text{-}butane]}$, so halving the concentration of isobutane means that the n-butane concentration must also decrease by about half if the system is to maintain equilibrium.

Exercise 15.7.1

Write an equilibrium constant expression for each reaction. What must happen to the concentration of the substance in bold when the indicated change occurs if the system is to maintain equilibrium?

a. $\mathrm{HBr\,(g) + NaH\,(s)} \rightleftharpoons \mathrm{NaBr\,(s) + \mathbf{H_2(g)}}$: the concentration of HBr is decreased by a factor of 3.
b. $\mathrm{6\,Li\,(s) + \mathbf{N_2(g)} \rightleftharpoons 2\,Li_3N\,(s)}$: the amount of Li is tripled.
c. $\mathrm{\mathbf{SO_2(g)} + Cl_2\,(g)} \rightleftharpoons \mathrm{SO_2Cl_2\,(l)}$: the concentration of $\mathrm{Cl_2}$ is doubled.

Answer a available at the end of this section.

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Le Chatelier's Principle (Changes in Temperature):

Le Chatelier's Principle (Changes in Temperature)(opens in new window) [youtu.be]

Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations. The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)} \rightleftharpoons \mathrm{2\,NH_3\,(g)} \tag{15.7.9}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements (Equation 15.7.9). The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.



Figure 15.7.1: The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen ($\mathrm{N_2}$) is nutritionally unavailable to a majority of plants due the tremendous stability of the nitrogen-nitrogen triple bond. Therefore, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation). Legumes achieve this conversion at ambient temperature by exploiting bacteria equipped with suitable enzymes.

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Footnotes

1. 1 Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle
: when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium
: concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress
: change to a reaction's conditions that may cause a shift in the equilibrium

Contributors and Attributions

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Answers

Exercise 15.7.1

$K = \frac{[H_2]}{[HBr]}$; $[H_2]$ must decrease by about a factor of 3.

$K = \frac{1}{[N_2]}$; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.

$K = \frac{1}{[SO_2][Cl_2]}$; $[SO_2]$ must decrease by about half.

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15.E: Exercises

15.1: The Concept of Equilibrium

Conceptual Problems

1. What is meant when a reaction is described as “having reached equilibrium”? What does this statement mean regarding the forward and reverse reaction rates? What does this statement mean regarding the amounts or concentrations of the reactants and the products?
2. Is it correct to say that the reaction has “stopped” when it has reached equilibrium? Explain your answer and support it with a specific example.
3. Why is chemical equilibrium described as a dynamic process? Describe this process in the context of a saturated solution of $NaCl$ in water. What is occurring on a microscopic level? What is happening on a macroscopic level?
4. Which of these systems exists in a state of chemical equilibrium?
   a. oxygen and hemoglobin in the human circulatory system
   b. iodine crystals in an open beaker
   c. the combustion of wood
   d. the amount of $^{14}\mathrm{C}$ in a decomposing organism

Conceptual Answer

1. When a reaction is described as "having reached equilibrium" this means that the forward reaction rate is now equal to the reverse reaction rate. In regards to the amounts or concentrations of the reactants and the products, there is no change due to the forward reaction rate being equal to the reverse reaction rate.

2. It is not correct to say that the reaction has "stopped" when it has reached equilibrium because it is not necessarily a static process where it can be assumed that the reaction rates cancel each other out to equal zero or be "stopped" but rather a dynamic process in which reactants are converted to products at the same rate products are converted to reactants. For example, a soda has carbon dioxide dissolved in the liquid and carbon dioxide between the liquid and the cap that is constantly being exchanged with each other. The system is in equilibrium and the reaction taking place is: $CO_2\ (g) + 2\ H_2O\ (l) \rightleftharpoons H_2CO_3\ (aq)$.

3. Chemical equilibrium is described as a dynamic process because there is a movement in which the forward and reverse reactions occur at the same rate to reach a point where the amounts or concentrations of the reactants and products are unchanging with time. Chemical equilibrium can be described in a saturated solution of $NaCl$ as on the microscopic level Na^+ and Cl^- ions continuously leave the surface of an $NaCl$ crystal to enter the solution, while at the same time Na^+ and Cl^- ions in solution precipitate on the surface of the crystal. At the macroscopic level, the salt can be seen to dissolve or not dissolve depending whether chemical equilibrium was established.

4.

a. Exists in a state of equilibrium as the chemical reaction that occurs in the body is: $Hb\ (aq) + 4\ H_2O\ (l) \rightleftharpoons Hb(O_2)_4\ (aq)$.

b. Exists in a state of equilibrium as the chemical reaction occurs is: $H_2\ (g) + I_2\ (g) \rightleftharpoons 2\ HI\ (g)$

c. Does not exist in a state of equilibrium as it is not a reversible process. The chemical reaction that takes place is: $6\ C_{10}H_{15}O_7\ (s) + heat \rightarrow C_{50}H_{10}O\ (s) + 10\ CH_2O\ (g)$.

d. Does not exist in a state of chemical equilibrium as it is not a reversible process. The chemical reaction that takes place is: $CH_2O + O_2 \rightarrow H_2O\ (l) + CO_2\ (g) + nutrients$.

15.2: The Equilibrium Constant

Conceptual Problems

1. For an equilibrium reaction, what effect does reversing the reactants and products have on the value of the equilibrium constant?
2. Which of the following equilibriums are homogeneous and which are heterogeneous?
   a. $2\ HF\ (g) \rightleftharpoons H_2\ (g) + F_2\ (g)$
   b. $C\ (s) + 2\ H_2\ (g) \rightleftharpoons CH_4\ (g)$
   c. $H_2C = CH_2\ (g) + H_2\ (g) \rightleftharpoons C_2H_6\ (g)$
   d. $2\ Hg\ (l) + O_2\ (g) \rightleftharpoons 2\ HgO\ (s)$
3. Classify each equilibrium system as either homogeneous or heterogeneous.
   a. $NH_4CO_2NH_2\ (s) \rightleftharpoons 2NH_3\ (g) + CO_2\ (g)$
   b. $C\ (s) + O_2\ (g) \rightleftharpoons CO_2\ (g)$
   c. $2\ Mg\ (s) + O_2\ (g) \rightleftharpoons 2\ MgO\ (s)$
   d. $AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$
4. If an equilibrium reaction is endothermic, what happens to the equilibrium constant if the temperature of the reaction is increased? if the temperature is decreased?
5. Industrial production of NO by the reaction $N_2\ (g) + O_2\ (g) \rightleftharpoons 2\ NO\ (g)$ is carried out at elevated temperatures to drive the reaction toward the formation of the product. After sufficient product has formed, the reaction mixture is quickly cooled. Why?
6. How would you differentiate between a system that has reached chemical equilibrium and one that is reacting so slowly that changes in concentration are difficult to observe?
7. What is the relationship between the equilibrium constant, the concentration of each component of the system, and the rate constants for the forward and reverse reactions?
8. Write the equilibrium constant expressions for K and K_p for each reaction.
   a. $CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$
   b. $PCl_3\ (g) + Cl_2\ (g) \rightleftharpoons PCl_5\ (g)$
   c. $2\ O_3\ (g) \rightleftharpoons 3\ O_2\ (g)$
9. Write the equilibrium constant expressions for K and K_p as appropriate for each reaction.
   a. $2\ NO\ (g) + O_2\ (g) \rightleftharpoons 2\ NO_2\ (g)$
   b. $\frac{1}{2}\ H_2\ (g) + 12\ I_2\ (g) \rightleftharpoons HI\ (g)$
   c. $cis - stilbene\ (soln) \rightleftharpoons trans - silbene\ (soln)$
10. Why is it incorrect to state that pure liquids, pure solids, and solvents are not part of an equilibrium constant expression?
11. Write the equilibrium constant expressions for K and K_p for each equilibrium reaction.
    a. $2\ S\ (s) + 3\ O_2\ (g) \rightleftharpoons 2\ SO_3\ (g)$
    b. $C\ (s) + CO_2\ (g) \rightleftharpoons 2\ CO\ (g)$
    c. $2\ ZnS\ (s) + 3\ O_2\ (g) \rightleftharpoons 2\ ZnO\ (s) + 2\ SO_2\ (g)$
12. Write the equilibrium constant expressions for K and K_p for each equilibrium reaction.
    a. $2\ HgO\ (s) \rightleftharpoons 2\ Hg\ (l) + O_2\ (g)$
    b. $H_2\ (g) + I_2\ (s) \rightleftharpoons 2\ HI\ (g)$
    c. $NH_4CO_2NH_2\ (s) \rightleftharpoons 2\ NH_3\ (g) + CO_2\ (g)$
13. At room temperature, the equilibrium constant for the reaction $2\ A\ (g) \rightleftharpoons B\ (g)$ is 1. What does this indicate about the concentrations of A and B at equilibrium? Would you expect K and K_p to vary significantly from each other? If so, how would their difference be affected by temperature?
14. For a certain series of reactions, if $\frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} = K_1$ and $\frac{[OH^-][H_2CO_3]}{[HCO_3^-]} = K_2$, what is the equilibrium constant expression for the overall reaction? Write the overall equilibrium equation.
15. In the equation for an enzymatic reaction, ES represents the complex formed between the substrate S and the enzyme protein E. In the final step of the following oxidation reaction, the product P dissociates from the ESO_2 complex, which regenerates the active enzyme:

$$E + S \rightleftharpoons ES\ \ K_1 \tag{15.E.1}$$

$$ES + O_2 \rightleftharpoons ESO_2 \;\; K_2 \tag{15.E.2}$$

$$ESO_2 \rightleftharpoons E + P \;\; K_3 \tag{15.E.3}$$

Give the overall reaction equation and show that $K = K_1 \times K_2 \times K_3$.

Conceptual Answers

1. By reversing the reactants and products for an equilibrium reaction, the equilibrium constant becomes: $K' = \frac{1}{K}$.

2.

a. This equilibrium is homogenous as all substances are in the same state.

b. This equilibrium is heterogeneous as not all substances are in the same state.

c. This equilibrium is homogeneous as all substances are in the same state.

d. This equilibrium is heterogeneous as not all substances are in the same state.

3.

a. This equilibrium is heterogeneous as not all substances are in the same state.

b. This equilibrium is heterogeneous as not all substances are in the same state.

c. This equilibrium is heterogeneous as not all substances are in the same state.

d. This equilibrium is heterogeneous as not all substances are in the same state.

4. According to Le Chatelier's principle, equilibrium will shift in the direction to counteract the effect of a constraint (such as concentration of a reactant, pressure, and temperature). Thus, in an endothermic reaction, the equilibrium shifts to the right-hand side when the temperature is increased which increases the equilibrium constant and the equilibrium shifts to the left-hand side when the temperature is decreased which decreases the equilibrium constant.

5. After sufficient industrial production of NO by the reaction of $N_2\ (g) + O_2\ (g) \rightleftharpoons 2\ NO\,(g)$ at elevated temperatures to drive the reaction toward the formation of the product, the reaction mixture is cooled quickly because it quenches the reaction and prevents the system from reverting to the low-temperature equilibrium composition that favors the reactants.

6. To differentiate between a system that has reached equilibrium and one that is reacting slowly that changes in concentrations are difficult to observe we can use Le Chatelier's principle to observe any shifts in the reaction upon addition of a constraint (such as concentration, pressure, or temperature).

7. The relationship between the equilibrium constant, the concentration of each component of a system, and the rate constants for the forward and reverse reactions considering a reaction of a general form: $a\ A + b\ B \rightleftharpoons c\ C + d\ D$ is $K = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_f}{k_r}$

8.

a.

$$K = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

$$K_p = \frac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})}$$

b.

$$K = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

$$K_p = \frac{(P_{PCl_5})}{(P_{Cl_3})(P_{Cl_2})}$$

c.

$$K = \frac{[O_2]^3}{[O_3]^2}$$

$$K_p = \frac{(P_{O_2})^3}{(P_{O_3})^2}$$

9.

a.

$$K = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$K_p = \frac{(P_{NO_2})^2}{(P_{NO})^2(P_{O_2})}$$

b.

$$K = \frac{[HI]}{[H_2]\frac{1}{2}[O_2]}$$

$$K_p = \frac{(P_{HI})}{(P_{H_2})^{\frac{1}{2}}(P_{O_2})}$$

c.

$$K = \frac{trans - stilbene}{cis - stilbene}$$

$$K_p = \frac{(P_{trans-stilbene})}{(P_{cis-stilbene})}$$

10. It is incorrect to state that pure liquids, pure solids, and solvents are not part of an equilibrium constant expression because they are not reactive enough or cause a change in the concentrations of the ions or the species that exist in the gas phase.

11.

a.

$$K = \frac{[SO_3]^2}{[O_2]^3}$$

$$K_p = \frac{(P_{SO_3})^2}{(P_{O_2})^3}$$

b.

$$K = \frac{[CO]^2}{[CO_2]}$$

$$K_p = \frac{(P_{CO})^2}{(P_{CO_2})}$$

c.

$$K = \frac{[SO_2]^2}{[O_2]^3}$$

$$K_p = \frac{(P_{SO_2})^2}{(P_{O_2})^3}$$

12.

a.

$$K = [O_2]$$

$$K_p = (P_{O_2})$$

b.

$$K = \frac{[HI]^2}{[H_2]}$$

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})}$$

c.

$$K = [NH_3]^2[CO_2]$$

$$K_p = (P_{NH_3})^2(P_{CO_2})$$

13.

$$K = \frac{[B]}{[A]^2} \rightarrow 1 = \frac{[B]}{[A]^2} \rightarrow [A]^2 = [B] \rightarrow [A] = \sqrt{B}$$

K and K_p vary by RT, but it largely depends on T as R is constant. A raise or decrease in temperature would cause a difference.

$$K_p = K(RT)^{\Delta n} = K(RT)^{-1} = \frac{K}{RT}$$

$$\Delta n = (total\ moles\ of\ gas\ on\ the\ product\ side) - (total\ of\ moles\ on\ the\ reactant\ side) = 1 - 2 = -1$$

14.

$$K = \frac{K_1}{K_2} = \frac{\frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]}}{\frac{[OH^-][H_2CO_3]}{[HCO_3^-]}} = \frac{[HCO_3^-]^2}{[CO_3^{2-}][H_2CO_3]}$$

$$CO_3^{2-}\ (g) + H_2CO_3\ (g) \rightleftharpoons 2\ HCO_3^-\ (g)$$

15.

$$K = K_1 \times K_2 \times K_3 = \frac{[ES]}{[E][S]} \times \frac{[ESO_2]}{[ES][O_2]} \times \frac{[E][P]}{[ESO_2]} = \frac{[P]}{[S][O_2]}$$

$$S + O_2 \rightleftharpoons P$$

Numerical Problems

1. Explain what each of the following values for K tells you about the relative concentrations of the reactants versus the products

in a given equilibrium reaction: $K = 0.892$; $K = 3.25 \times 10^{8}$; $K = 5.26 \times 10^{-11}$. Are products or reactants favored at equilibrium?

2. Write the equilibrium constant expression for each reaction. Are these equilibrium constant expressions equivalent? Explain.
   a. $N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$
   b. $\frac{1}{2}\ N_2O_4\ (g) \rightleftharpoons NO_2\ (g)$
3. Write the equilibrium constant expression for each reaction.
   a. $\frac{1}{2}N_2\ (g) + \frac{3}{2}H_2\ (g) \rightleftharpoons NH_3\ (g)$
   b. $\frac{1}{3}N_2\ (g) + H_2\ (g) \rightleftharpoons \frac{2}{3}NH_3\ (g)$

How are these two expressions mathematically related to the equilibrium constant expression for

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)? \tag{15.E.4}$$

4. Write an equilibrium constant expression for each reaction.
   a. $C\ (s) + 2\ H_2O\ (g) \rightleftharpoons CO_2\ (g) + 2\ H_2\ (g)$
   b. $SbCl_3\ (g) + Cl_2\ (g) \rightleftharpoons SbCl_5\ (g)$
   c. $2\ O_3\ (g) \rightleftharpoons 3\ O_2\ (g)$
5. Give an equilibrium constant expression for each reaction.

a. $2\ NO\ (g) + O_2\ (g) \rightleftharpoons 2\ NO_2\ (g)$

b. $\frac{1}{2}H_2\ (g) + \frac{1}{2}I_2\ (g) \rightleftharpoons HI\ (g)$

c. $CaCO_3\ (s) + 2\ HOCl\ (aq) \rightleftharpoons Ca^{2+}\ (aq) + 2\ OCl^-\ (aq) + H_2O\ (l) + CO_2\ (g)$

6. Calculate K and K_p for each reaction.

a. $2\ NOBr\ (g) \rightleftharpoons 2\ NO\ (g) + Br_2\ (g)$: at 727°C, the equilibrium concentration of NO is 1.29 M, Br_2 is 10.52 M, and $NOBr$ is 0.423 M.
b. $C\ (s) + CO_2\ (g) \rightleftharpoons 2\ CO\ (g)$: at 1,200 K, a 2.00 L vessel at equilibrium has partial pressures of 93.5 atm CO_2 and 76.8 atm CO, and the vessel contains 3.55 g of carbon.

7. Calculate K and K_p for each reaction.

a. $N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$: at the equilibrium temperature of –40°C, a 0.150 M sample of N_2O_4 undergoes a decomposition of 0.456%.
b. $CO\ (g) + 2\ H_2\ (g) \rightleftharpoons CH_3OH\ (g)$: an equilibrium is reached at 227°C in a 15.5 L reaction vessel with a total pressure of 6.71×10^2 atm. It is found to contain 37.8 g of hydrogen gas, 457.7 g of carbon monoxide, and 7,193 g of methanol.

8. Determine K and K_p (where applicable) for each reaction.

a. $2\ H_2S\ (g) \rightleftharpoons 2\ H_2\ (g) + S_2\ (g)$: at 1065°C, an equilibrium mixture consists of 1.00×10^{-3} M H_2, 1.20×10^{-3} M S_2, and 3.32×10^{-3} M H_2S.
b. $Ba(OH)_2\ (s) \rightleftharpoons 2\ OH^-\ (aq) + Ba^{2+}\ (aq)$: at 25°C, a 250 mL beaker contains 0.330 mol of barium hydroxide in equilibrium with 0.0267 mol of barium ions and 0.0534 mol of hydroxide ions.

9. Determine K and K_p for each reaction.

a. $2\ NOCl\ (g) \rightleftharpoons 2\ NO\ (g) + Cl_2\ (g)$: at 500 K, a 24.3 mM sample of $NOCl$ has decomposed, leaving an equilibrium mixture that contains 72.7% of the original amount of $NOCl$.
b. $Cl_2\ (g) + PCl_3\ (g) \rightleftharpoons PCl_5\ (g)$: at 250°C, a 500 mL reaction vessel contains 16.9 g of Cl_2 gas, 0.500 g of PCl_3, and 10.2 g of PCl_5 at equilibrium.

10. The equilibrium constant expression for a reaction is $\dfrac{[CO_2]^2}{[SO_2]^2[O_2]}$. What is the balanced chemical equation for the overall reaction if one of the reactants is $Na_2CO_3\ (s)$?

11. The equilibrium constant expression for a reaction is $\dfrac{[NO][H_2O]^{\frac{3}{2}}}{[NH_3][O_2]^{\frac{5}{4}}}$. What is the balanced chemical equation for the overall

reaction?

12. Given $K = \frac{k_f}{k_r}$, what happens to the magnitude of the equilibrium constant if the reaction rate of the forward reaction is doubled? What happens if the reaction rate of the reverse reaction for the overall reaction is decreased by a factor of 3?

13. The value of the equilibrium constant for

$$2\,H_2\,(g) + S_2\,(g) \rightleftharpoons 2\,H_2S\,(g) \tag{15.E.5}$$

is 1.08×10^7 at 700°C. What is the value of the equilibrium constant for the following related reactions

a. $H_2\ (g) + 12\ S_2\ (g) \rightleftharpoons H_2S\ (g)$
b. $4\ H_2\ (g) + 2\ S_2\ (g) \rightleftharpoons 4\ H_2S\ (g)$
c. $H_2S\ (g) \rightleftharpoons H_2\ (g) + 12\ S_2\ (g)$

Numerical Answers

1. In the given equilibrium reaction where $K = 0.892 \approx 1$ has a concentration of the reactants that is approximately equal to the concentration of the products so neither formation of the reactants or products is favored. In the given equilibrium reaction where $K = 3.25 \times 10^8 > 1$ has a concentration of the products that is relatively small compared to the concentration of the reactants so the formation of the products is favored. In the given equilibrium reaction where $K = 5.26 \times 10^{-11} < 1$ has a concentration of products that is relatively large compared to that of the concentration of the reactants so the formation of the reactants is favored.

2.

a. $K = \frac{[NO_2]^2}{[N_2O_4]}$

b. $K = \frac{[NO_2]}{[N_2O_4]^{\frac{1}{2}}}$

Although the equilibrium constant expressions have a 2:1 ratio of concentration for the products to the concentration of the reactants for the same species involved to get the K value for a. We would need to square it to get the K value for b.

3.

a. $K' = \frac{[NH_3]}{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}$

b. $K'' = \frac{[NH_3]^{\frac{2}{3}}}{[N_2]^{\frac{1}{2}}[H_2]}$

$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$

$K' = K^{\frac{1}{2}}$

$K'' = K^{\frac{1}{3}}$

4.

a. $K = \frac{[H_2]^2[CO_2]}{[H_2O]^2}$

b. $K = \dfrac{[SbCl_5]}{[SbCl_3][Cl_2]}$

c. $K = \dfrac{[O_2]^3}{[O_3]^2}$

5.

a. $K = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$

b. $K = \dfrac{[HI]}{[H_2]^{\frac{1}{2}}[I_2]^{\frac{1}{2}}}$

c. $K = \dfrac{[Ca^{2+}][OCl^-]^2[CO_2]}{[HOCl]^2}$

6.

a.

$K = \dfrac{[NO]^2[Br]}{[NOBr]^2} = \dfrac{[1.29\ M]^2[10.52\ M]}{[0.423\ M]^2} = 97.8$

$K_p = K(RT)^{\Delta n} = (97.8)((0.08206\frac{L \cdot atm}{mol \cdot K})((727 + 273.15)K))^{3-2} = 8.03x10^4$

b.

$K_p = K(RT)^{\Delta n} = K(RT)^{2-1} = K(RT) \rightarrow K = \dfrac{K_p}{RT} = \dfrac{63.1}{(0.08206\frac{L \cdot atm}{mol \cdot K})(1{,}200\ K)} = 6.41$

$K = \dfrac{(P_{CO})^2}{P_{CO_2}} = \dfrac{(76.8\ atm)^2}{93.5\ atm} = 63.1$

7.

a.

$K = \dfrac{[NO_2]^2}{[N_2O_4]} = \dfrac{[0.001368\ M]}{[0.149316\ M]} = 1.25x10^{-5}$

$[NO_2] = (2)(0.150\ M)(0.00456) = 0.001368\ M$

$[N_2O_4] = (0.150\ M)(1 - 0.00456) = 0.149316\ M$

$K_p = K(RT)^{\Delta n} = (1.25x10^{-5})((0.08206\frac{L \cdot atm}{mol \cdot K})((-40 + 273.15)K))^{2-1} = 2.39x10^{-4}$

b.

$K = \dfrac{[CH_3OH]}{[CO][H_2]^2} = \dfrac{[14.5\ M]}{[1.05\ M][1.21\ M]^2} = 9.47$

$[CH_3OH] = 7,193\ g\ CH_3OH \times \frac{1\ mol\ CH_3OH}{32.04\ g\ CH_3OH} \times \frac{1}{15.5\ L} = 14.5\ M$

$[CO] = 457.7\ g\ CO \times \frac{1\ mol\ CO}{28.01\ g\ CO} \times \frac{1}{15.5\ L} = 1.05\ M$

$[H_2] = 37.8\ g\ H_2 \times \frac{1\ mol\ H_2}{2.02\ g\ H_2} \times \frac{1}{15.5\ L} = 1.21\ M$

$K_p = K(RT)^{\Delta n} = (9.47)((0.08206\frac{L \cdot atm}{mol \cdot K})((227 + 273.15)K))^{1-3} = 5.62x10^{-2}$

8.

a.

$K = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{[1.00\times10^{-3}\ M]^2[1.20\times10^{-3}\ M]}{[3.32\times\ 10^{-3}\ M]^2} = 1.09 \times 10^{-4}$

$K_p = K(RT)^{\Delta n} = (1.09 \times 10^{-4})((0.08206\frac{L\cdot atm}{mol\cdot K})((1065 + 273.15)K))^{3-2} = 1.20 \times 10^{-2}$

b.

$K = [OH^-]^2[Ba^{2+}] = [0.2136\,M]^2[0.1068\ M] = 4.87 \times 10^{-3}$

$[OH^-] = 0.0534\ mol\ OH^- \times \frac{1}{0.25\ L} = 0.2136\ M$

$[Ba^{2+}] = 0.0267\ mol\ Ba^{2+} \times \frac{1}{0.25\ L} = 0.1068\ M$

$K_p = K(RT)^{\Delta n} = (4.87 \times 10^{-3})((0.08206\frac{L\cdot atm}{mol\cdot K})((25 + 273.15)K))^{3-1} = 2.92$

9.

a.

$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = 4.59 \times 10^{-4}$

$K_p = K(RT)^{\Delta n} = (4.59 \times 10^{-4})((0.08206\frac{L\cdot atm}{mol\cdot K})(500K))^{3-2} = 1.88 \times 10^{-2}$

b.

$K = \frac{[PCl_5]}{[Cl_2][PCl_3]} = \frac{[9.80\times10^{-2}\ M]}{[4.77\times10^{-1}\ M][7.28\times10^{-3}\ M]} = 28.2$

$[PCl_5] = 10.2\ g\ PCl_5 \times \frac{1\ mol\ PCl_5}{208.2388\ g\ PCl_5} \times \frac{1}{0.5\ L} = 9.80 \times 10^{-2}\ M$

$[Cl_2] = 16.9\ g\ Cl_2 \times \frac{1\ mol\ Cl_2}{70.9\ g\ Cl_2} \times \frac{1}{0.5\ L} = 4.77 \times 10^{-1}\ M$

$[PCl_3] = 0.500\ g\ PCl_3 \times \frac{1\ mol\ PCl_3}{137.33\ g\ PCl_3} \times \frac{1}{0.5\ L} = 7.28 \times 10^{-3}\ M$

$K_p = K(RT)^{\Delta n} = (28.2)((0.08206\frac{L\cdot atm}{mol\cdot K})(250 + 273.15)K)^{1-2} = 6.57 \times 10^{-1}$

10. $2\ SO_2\ (g) + O_2\ (g) + 2\ Na_2CO_3\ (s) \rightleftharpoons 2\ CO_2\ (g) + 2\ Na_2SO_4\ (s)$

11. $NH_3\ (g) + \frac{5}{4}\ O_2\ (g) \rightleftharpoons NO\ (g) + \frac{3}{2}\ H_2O\ (g)$

12. If the reaction rate of the forward reaction is doubled the magnitude of the equilibrium constant is doubled. If the reaction rate of the reverse reaction for the overall reaction is described by a factor of 3 the magnitude of the equilibrium constant is increased by a factor of 3.

13. $K' = \frac{[H_2S]^2}{[H_2]^2[S_2]} = 1.08 \times 10^7$

a. $K = \frac{[H_2S]}{[H_2][S_2]^{\frac{1}{2}}} = K'^{\frac{1}{2}} = (1.08 \times 10^7)^{\frac{1}{2}} = 3.29 \times 10^3$ b. $K = \frac{[H_2S]^4}{[H_2]^4[S_2]^2} = K'^2 = (1.08 \times 10^7)^2 = 1.17 \times 10^{14}$ c. $K = \frac{[H_2][S_2]^{\frac{1}{2}}}{[H_2S]} = K'^{-\frac{1}{2}} = (1.08 \times 10^7)^{-\frac{1}{2}} = 3.04 \times 10^{-4}$

15.3: Interpreting & Working with Equilibrium Constants

Conceptual Problems

1. Describe how to determine the magnitude of the equilibrium constant for a reaction when not all concentrations of the substances are known.
2. Calculations involving systems with very small or very large equilibrium constants can be dramatically simplified by making

certain assumptions about the concentrations of products and reactants. What are these assumptions when K is (a) very large and (b) very small? Illustrate this technique using the system $A + 2B \rightleftharpoons C$ for which you are to calculate the concentration of the product at equilibrium starting with only A and B. Under what circumstances should simplifying assumptions not be used?

Conceptual Answers

1. The magnitude of the equilibrium constant for a reaction depends on the form in which the chemical reaction is written. For example, writing a chemical reaction in different but chemically equivalent forms causes the magnitude of the equilibrium constant to be different but can be related by comparing their respective magnitudes.

2.

a. When K is very large the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion.

$$K = \frac{[C]}{[A][B]^2} = \frac{[C]}{very\ small} = \frac{1}{0} = \infty \rightarrow [C] = \infty$$

b. When K is very small the reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of the reactants.

$$K = \frac{[C]}{[A][B]^2} = \frac{very\ small}{[A][B]^2} = \frac{0}{1} = 0 \rightarrow [C] = 0$$

Simplifying assumptions should not be used if the equilibrium constant is not known to be very large or very small.

Numerical Problems

Please be sure you are familiar with the quadratic formula before proceeding to the Numerical Problems.

1. In the equilibrium reaction $A + B \rightleftharpoons C$, what happens to K if the concentrations of the reactants are doubled? tripled? Can the same be said about the equilibrium reaction $2\ A \rightleftharpoons B + C$?
2. The following table shows the reported values of the equilibrium P_{O_2} at three temperatures for the reaction $Ag_2O\ (s) \rightleftharpoons 2\ Ag\ (s) + \frac{1}{2}\ O_2\ (g)$, for which ΔH° = 31 kJ/mol. Are these data consistent with what you would expect to occur? Why or why not?

T (°C)	$P_{O_2}\ (mmHg)$
150	182
184	143
191	126

3. Given the equilibrium system $N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$, what happens to K_p if the initial pressure of N_2O_4 is doubled? If K_p is 1.7×10^{-1} at 2300°C, and the system initially contains 100% N_2O_4 at a pressure of 2.6×10^2 atm, what is the equilibrium pressure of each component?
4. At 430°C, 4.20 mol of HI in a 9.60 L reaction vessel reaches equilibrium according to the following equation:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) \tag{15.E.6}$$

   At equilibrium, $[H_2] = 0.047\ M$ and $[HI] = 0.345\ M$ What are K and K_p for this reaction?
5. Methanol, a liquid used as an automobile fuel additive, is commercially produced from carbon monoxide and hydrogen at 300°C according to the following reaction:

$$CO\,(g) + 2\,H_2\,(g) \rightleftharpoons CH_3OH\,(g) \tag{15.E.7}$$

   with $K_p = 1.3 \times 10^{-4}$. If 56.0 g of CO is mixed with excess hydrogen in a 250 mL flask at this temperature, and the hydrogen pressure is continuously maintained at 100 atm, what would be the maximum percent yield of methanol? What pressure of hydrogen would be required to obtain a minimum yield of methanol of 95% under these conditions?
6. Starting with pure A, if the total equilibrium pressure is 0.969 atm for the reaction $A\ (s) \rightleftharpoons 2\ B\ (g) + C\ (g)$, what is K_p?

7. The decomposition of ammonium carbamate to NH_3 and CO_2 at 40°C is written as $NH_4CO_2NH_2\ (s) \rightleftharpoons 2\ NH_3\ (g) + CO_2\ (g)$. If the partial pressure of NH_3 at equilibrium is 0.242 atm, what is the equilibrium partial pressure of CO_2? What is the total gas pressure of the system? What is K_p?
8. At 375 K, K_p for the reaction $SO_2Cl_2\ (g) \rightleftharpoons SO_2\ (g) + Cl_2\ (g)$ is 2.4, with pressures expressed in atmospheres. At 303 K, K_p is 2.9×10^{-2}.
   a. What is K for the reaction at each temperature?
   b. If a sample at 375 K has 0.100 M Cl_2 and 0.200 M SO_2 at equilibrium, what is the concentration of SO_2Cl_2?
   c. If the sample given in part b is cooled to 303 K, what is the pressure inside the bulb?
9. For the gas-phase reaction $a\ A \rightleftharpoons b\ B$, show that $K_p = K(RT)^{\Delta n}$ assuming ideal gas behavior.
10. For the gas-phase reaction $I_2 \rightleftharpoons 2\ I$, show that the total pressure is related to the equilibrium pressure by the following equation:

$$P_T = \sqrt{K_p P_{I_2}} + P_{I_2} \tag{15.E.8}$$

11. Experimental data on the system $Br_2\ (l) \rightleftharpoons Br_2\ (aq)$ are given in the following table. Graph $Br_2\ (aq)$ versus moles of $Br_2\ (l)$ present; then write the equilibrium constant expression and determine K.

Grams Br_2 in 100 mL Water	Br_2 (M)
1.0	0.0626
2.5	0.156
3.0	0.188
4.0	0.219
4.5	0.219

12. Data accumulated for the reaction (\n-butane(g) \rightleftharpoons isobutane(g)\) at equilibrium are shown in the following table. What is the equilibrium constant for this conversion? If 1 mol of n-butane is allowed to equilibrate under the same reaction conditions, what is the final number of moles of n-butane and isobutane?

Moles n-butane	Moles Isobutane
0.5	1.25
1.0	2.5
1.50	3.75

13. Solid ammonium carbamate ($NH_4CO_2NH_2$) dissociates completely to ammonia and carbon dioxide when it vaporizes: $NH_4CO_2NH_2\ (s) \rightleftharpoons 2\ NH_3\ (g) + CO_2\ (g)$ At 25°C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium partial pressure of each gas? What is K_p? If the concentration of CO_2 is doubled and then equilibrates to its initial equilibrium partial pressure +x atm, what change in the NH_3 concentration is necessary for the system to restore equilibrium?
14. The equilibrium constant for the reaction $COCl_2\ (g) \rightleftharpoons CO\ (g) + Cl_2\ (g)$ is $K_p = 2.2 \times 10^{-10}$ at 100°C. If the initial concentration of $COCl_2$ is $3.05 \times 10^{-3}\ M$, what is the partial pressure of each gas at equilibrium at 100°C? What assumption can be made to simplify your calculations?
15. Aqueous dilution of IO_4^- results in the following reaction:

$$IO_4^-\,(aq) + 2\,H_2O(l) \rightleftharpoons H_4IO_6^-\,(aq) \tag{15.E.9}$$

with $K = 3.5 \times 10^{-2}$. If you begin with 50 mL of a 0.896 M solution of IO_4^- that is diluted to 250 mL with water, how many moles of $H_4IO_6^-$ are formed at equilibrium?
16. Iodine and bromine react to form IBr, which then sublimes. At 184.4°C, the overall reaction proceeds according to the following equation:

$$I_2\,(g) + Br_2\,(g) \rightleftharpoons 2\,IBr\,(g) \tag{15.E.10}$$

with $K_p = 1.2 \times 10^2$. If you begin the reaction with 7.4 g of I_2 vapor and 6.3 g of Br_2 vapor in a 1.00 L container, what is the concentration of $IBr\ (g)$ at equilibrium? What is the partial pressure of each gas at equilibrium? What is the total pressure of the system?
17. For the reaction

$$2\,C\,(s) + N_2\,(g) + 5\,H_2 \rightleftharpoons 2\,CH_3NH_2\,(g) \tag{15.E.11}$$

with $K = 1.8 \times 10^{-6}$. If you begin the reaction with 1.0 mol of N_2, 2.0 mol of H_2, and sufficient $C\ (s)$ in a 2.00 L container, what are the concentrations of N_2 and CH_3NH_2 at equilibrium? What happens to K if the concentration of H_2 is doubled?

Numerical Answers

1. In both cases, the equilibrium constant will remain the same as it does not depend on the concentrations.

2. No, the data is not consistent with what I would expect to occur because enthalpy is positive indicating that the reaction is endothermic thus heat is on the left side of the reaction. As the temperature is raised P_{O_2} would be expected to increase to counteract the constraint.

3.

If the initial pressure of N_2O_4 was doubled then K_p is one half of the original value.

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} \rightarrow 1.7 \times 10^{-1} = \frac{(2x)^2}{2.6\times10^2 - x} \rightarrow 44.2 - 0.17x = 4x^2 \rightarrow x \approx 3.303\ atm$$

	$P_{N_2O_4}$	P_{NO_2}
I	2.6×10^2	0
C	-x	+2x
E	$2.6 \times 10^2 - x$	2x

$P_{N_2O_4} = 2.6 \times 10^2 - x = 260 - 3.303 = 2.6 \times 10^2\ atm$

$P_{NO_2} = 2x = (2)(3.303) = 6.6\ atm$

4.

$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.345\ M}{(0.047\ M)(0.047\ M)} = 157$

$K_p = K(RT)^{\Delta n} = (157)((0.08206\frac{L\cdot atm}{mol\cdot K})(430 + 273.15)K)^{2-2} = 157$

5.

$Maximum\ \ Percent\ \ Yield = \frac{Actual}{Theoretical} \times 100\% = \frac{212.593}{376.127} \times 100\% = 56.52\% \approx 57\%$

$PV = nRT \rightarrow P = \frac{(1.999\ mol)(0.08206\frac{L\cdot atm}{mol\cdot K})(300+273.15)K}{0.250\ L} = 376.127\ atm$

$[CO] = 56.0\ g\ CO \times \frac{1\ mol\ CO}{28.01\ g\ CO} = 1.999\ mol\ CO$

$K_p = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2} \rightarrow 1.3 \times 10^{-4} = \frac{x}{(376.02-x)(100^2)} \rightarrow 1.3 = \frac{x}{376.07-x} \rightarrow 488.965 - 1.3x = x \rightarrow 488.965 = 2.3x \rightarrow x = 212.593\ atm$

$K_p = \frac{(P_{CH_3OH})}{(P_{CO})(P_{H_2})^2} \rightarrow 1.3 \times 10^{-4} = \frac{357.320}{(376.127-357.320)(P_{H_2})^2} \rightarrow 1.3 \times 10^{-4} = \frac{357.320}{(18.80635)(P_{H_2})^2} \rightarrow 0.002444(P_{H_2})^2 = 357.320 \rightarrow (P_{H_2}) = 382.300 \approx 3.8 \times 10^2\ atm$

$Minimum\ \ Percent\ \ Yield = \frac{Actual}{Theoretical} \times 100\% \rightarrow 95\% = \frac{x}{376.127} \times 100\% \rightarrow x = 357.320\ atm$

	CO	$2\ H_2$	CH_3OH
I	376.127	100	0
C	-x	-2x	+x
E	376.127-x	100 (maintained)	x

6. $K_p = \frac{(P_B)^2(P_C)}{P_A} = \frac{[2x]^2[x]}{[0.969-x]} = \frac{4x^3}{0.969-x}$

	A	$2\ B$	C
I	0.969	0	0
C	-x	+2x	+x
E	0.969-x	2x	x

7.

$P_{CO_2} = P_{tot} - P_{NH_3} = P_{tot} - 0.242\ atm$

$P_{tot} = P_{NH_3} + P_{CO_2} = 0.242\ atm + P_{CO_2}$

$K_p = (P_{NH_3})^2(P_{CO_2}) = (0.242\,atm)^2(P_{CO_2})$

8.

a.

$At\ 375\ K: K_p = K(RT)^{\Delta n} \rightarrow K = \frac{K_p}{(RT)^{\Delta n}} = \frac{2.9\times10^{-2}}{((0.08206\frac{L\cdot atm}{mol\cdot K})(375\ K))^{2-1}} = 7.80\times10^{-2}$

$At\ 303\ K: K_p = K(RT)^{\Delta n} \rightarrow K = \frac{K_p}{(RT)^{\Delta n}} = \frac{2.9\times10^{-2}}{((0.08206\frac{L\cdot atm}{mol\cdot K})(303\ K))^{2-1}} = 1.17\times10^{-3}$

b. $K = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} \rightarrow [SO_2Cl_2] = \frac{[0.200\ M][0.100\ M]}{7.80\times10^{-2}} = 2.56\times10^{-1}\ M$

c. If the sample given in part b is cooled to 303 K, the pressure inside the bulb would decrease.

9.

$K_p = \frac{(P_B)^b}{(P_A)^a} = \frac{((\frac{n_B}{V})(RT))^b}{((\frac{n_A}{V})(RT))^a} = \frac{[B]^b(RT)^b}{[A]^a(RT)^a} = K(RT)^{b-a} = K(RT)^{\Delta n}$

$PV = nRT \rightarrow P = \frac{n}{V}RT$

$K = \frac{[B]^b}{[A]^a}$

$\Delta n = b - a$

10.

$P_T = P_I + P_{I_2} = \sqrt{K_p P_{I_2}} + P_{I_2}$

$K_p = \frac{(P_I)^2}{P_{I_2}} \rightarrow (P_I)^2 = K_p(P_{I_2}) \rightarrow P_I = \sqrt{K_p P_{I_2}}$

11.

The graph should be a positive linear correlation.

$Br_2\ (l)\ (M)\ (x-axis)$	$Br_2\ (aq)\ (M)\ (y-axis)\ (same\ value\ for\ K)$
$6.26\times10^{-}2$	0.0626
$1.56\times10^{-}1$	0.156
$1.88\times10^{-}2$	0.188
$2.50\times10^{-}2$	0.219

$Br_2\ (l)\ (M)\ (x-axis)$	$Br_2\ (aq)\ (M)\ (y-axis)\ (same\ value\ for\ K)$
$2.82 \times 10^{-}2$	0.219

$$[Br_2\ (l)] = 1.0\ g\ Br_2 \times \frac{1\ mol\ Br_2}{159.808\ g\ Br_2} \times \frac{1}{0.1\ L} = 6.26 \times 10^{-2}$$

$K = \frac{[Br_2\ (aq)]}{[Br_2\ (l)]} = \frac{[Br_2\ (aq)]}{1} = [Br_2\ (aq)]$

12. $K = \frac{[isobutane]}{[n-butane]} = \frac{x}{1-x}$

	$n-butane$	$isobutane$
I	1	0
C	-x	+x
E	1-x	x

13.

$P_{NH_3} = 2x = 2(0.0387) = 7.73 \times 10^{-2}\ atm$

$P_{CO_2} = x = 3.87 \times 10^{-2}\ atm$

$K_p = (P_{NH_3})^2(P_{CO_2}) = (2x)^2(x) = 4x^3 = 4(0.0387)^3 = 2.32 \times 10^{-4}$

$$P_{tot} = P_{NH_3} + P_{CO_2} \rightarrow 0.116 = 2x + x \rightarrow 0.116 = 3x \rightarrow x = 0.0387$$

If the concentration of CO_2 is doubled and then equilibrates to its initial equilibrium partial pressure +x atm, the concentration of NH_3 should also be doubled for the system to restore equilibrium.

	NH_3	CO_2
I	0	0
C	2x	x
E	2x	x

14.

$P_{COCl_2} = 9.34 \times 10^{-2} - x = 9.34 \times 10^{-2} - 9.34 \times 10^{-22} = 9.34 \times 10^{-2}\ atm$

$P_{CO} = x = 9.34 \times 10^{-22}\ atm$

$P_{Cl_2} = x = 9.34 \times 10^{-22}\ atm$

Assume that the equilibrium mainly lies on the reactants side because the K_p value is less than 1.

$$K_p = \frac{(P_{CO})(P_{Cl_2})}{(P_{COCl_2})} \rightarrow 2.2 \times 10^{-10} = \frac{x^2}{9.34 \times 10^{-2} - x} \rightarrow 2.0548 \times 10^{-11} - 2.2 \times 10^{-10}x = x^2 \rightarrow x^2 + 2.2 \times 10^{-10}x - 2.0548 \times 10^{-11} = 0$$
$$\rightarrow x = 9.34 \times 10^{-22}$$

$$PV = nRT \rightarrow P = \frac{nRT}{V} = (3.05 \times 10^{-3})(0.08206 \frac{L \cdot atm}{mol \cdot K})(100 + 273.15)K = 9.34 \times 10^{-2}$$

	$COCl_2$	CO	Cl_2
I	9.34×10^{-2}	0	0

	$COCl_2$	CO	Cl_2
C	-x	+x	+x
E	$9.34 \times 10^{-2} - x$	x	x

15. $[H_4IO_6^-] = x = 1.6 \times 10^{-3}\ mol$

$K = \frac{[H_4IO_6^-]}{[IO_4^-]} \rightarrow 3.5 \times 10^{-2} = \frac{x}{(0.0448-x)} \rightarrow x = 1.568 \times 10^{-3}$

$IO_4^- : 50\ mL\ IO_4^- \times \frac{1\ L\ IO_4^-}{1{,}000\ mL\ IO_4^-} \times \frac{0.896\ mol\ IO_4^-}{1\ L\ IO_4^-} = 0.0448\ mol$

	IO_4^-	$H_4IO_6^-$
I	0.0448	0
C	-x	+x
E	0.0448-x	x

16. $PV = nRT \rightarrow \frac{P}{RT} = \frac{n}{V} \rightarrow \frac{12.9468}{(0.08206\frac{L \cdot atm}{mol \cdot K})(184.4+273.15)K} = 3.5 \times 10^{-1}\ M$

$K_p = \frac{(P_{IBr})^2}{(P_{I_2})(P_{Br_2})} \rightarrow 1.2 \times 10^{-2} = \frac{2x}{(1.096-x)(1.479-x)} = \frac{2x}{x^2-2.575x+1.62098} \rightarrow 0.012x^2 - 0.0309x + 0.0194518 = 2x \rightarrow 0.012x^2 - 2.0309 + 0.0194518 = 0 \rightarrow x = 12.9468$

	I_2	Br_2	IBr
I	1.096	1.479	0
C	-x	-x	2x
E	1.096-x	1.479-x	2x

$PV = nRT \rightarrow P = \frac{nRT}{V} = (2.92 \times 10^{-2}\ M)(0.08206\frac{L \cdot atm}{mol \cdot K})(184.4 + 273.15)K = 1.096\ atm$

$[I_2] = 7.4\ g\ I_2 \times \frac{1\ mol\ I_2}{253\ g\ I_2} \times \frac{1}{1.00\ L} = 2.92 \times 10^{-2}\ M$

$PV = nRT \rightarrow P = nRTV = (3.94 \times 10^{-2}\ M)(0.08206\frac{L \cdot atm}{mol \cdot K})(184.4 + 273.15)K = 1.479\ atm$

$[Br_2] = 6.3\ g\ Br_2 \times \frac{1\ mol\ Br_2}{159.808\ g\ Br_2} = 3.94 \times 10^{-2}\ M$

17.

$[N_2] = 0.5 - 12x = 0.5 - 12(0.000471330) = 0.494\ M$

$[CH_3NH_2] = 2x = 2(0.0004713300 = 9.43 \times 10^{-4}\ M$

$If\ the\ concentration\ of\ H_2\ is\ doubled\ ,then\ K = \frac{[CH_3NH_2]^2}{[N_2][H_2]^5} = \frac{(9.43 \times 10^{-4})^2}{(0.494)(1.998)^5} = 5.65 \times 10^{-8}$

$2 \times [H_2] = 2(1.0 - 2.5x) = 2(1.0 - 2.5(0.000471330)) = 1.998\ M$

$K = \frac{[CH_3NH_2]^2}{[N_2][H_2]^5} \rightarrow 1.8 \times 10^{-6} = \frac{(2x)^2}{(0.5-x)(1.0-5x)^5} \rightarrow x = 0.000471330\ M$

	C	N_2	H_2	CH_3NH_2
I	-	0.5	1.0	0
C	-	-x	-5x	2x

	C	N_2	H_2	CH_3NH_2
E	-	0.5-x	1.0-5x	2x

$[N_2] = 1.00\ mol\ N_2 \times \frac{1}{2.00\ L} = 0.5\ M$

$[H_2] = 2.00\ mol\ H_2 \times \frac{1}{2.00\ L} = 1.0\ M$

15.4: Heterogeneous Equilibria

15.5: Calculating Equilibrium Constants

15.6: Applications of Equilibrium Constants

Conceptual Problems

1. During a set of experiments, graphs were drawn of [reactants] versus [products] at equilibrium. Using Figure 15.8 and Figure 15.9 as your guides, sketch the shape of each graph using appropriate labels.

a. $H_2O\ (l) \rightleftharpoons H_2O\ (g)$
b. $2\ MgO\ (s) \rightleftharpoons 2\ Mg\ (s) + O_2\ (g)$
c. $2\ O_3\ (g) \rightleftharpoons 3\ O_2\ (g)$
d. $2\ PbS\ (g) + 3\ O_2\ (g) \rightleftharpoons 2\ PbO\ (s) + 2\ SO_2\ (g)$

2. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

a. $2\ NaHCO_3\ (s) \rightleftharpoons Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (g)$: $[CO_2]$ is doubled.
b. $N_2F_4\ (g) \rightleftharpoons 2\ NF_2\ (g)$: $[NF_2]$ is decreased by a factor of 2.
c. $H_2\ (g) + I_2\ (g) \rightleftharpoons 2\ HI\ (g)$: $[I_2]$ is doubled.

3. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

a. $CS_2\ (g) + 4\ H_2\ (g) \rightleftharpoons CH_4\ (g) + 2\ H_2S\ (g)$: $[CS_2]$ is doubled.
b. $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$: $[Cl_2]$ is decreased by a factor of 2.
c. $4\ NH_3\ (g) + 5\ O_2\ (g) \rightleftharpoons 4\ NO\ (g) + 6\ H_2O\ (g)$: $[NO]$ is doubled.

Conceptual Answer

1.

a. According to Figure 15.8, we could obtain a graph with the x-axis labeled $[H_2O]\ (l)\ (M)$ and y-axis labeled $[H_2O]\ (g)\ (M)$. The graph should have a positive linear correlation. For any equilibrium concentration of $H_2O\ (g)$, there is only one equilibrium $H_2O\ (l)$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]\ (g)$ at equilibrium requires a large $[H_2O]\ (l)$ and vice versa. In this case, the slope of the line is equal to K.

b. According to Figure 15.9, we could obtain a graph with the x-axis labeled $[O2]\ (M)$ and y-axis labeled $[MgO]\ (M)$. Because $O_2\ (g)$ is the only one in gaseous form, the graph would depend on the concentration of O_2.

c. According to Figure 15.8, we could obtain a graph with the x-axis labeled $[O_3]\ (M)$ and y-axis labeled $[O2]\ (M)$. The graph should have a positive linear correlation. For every $3\ O_2\ (g)$ there is $2\ O_3\ (g)$. Because the magnitudes of the two concentrations are directly proportional, a large $[O3]\ (g)$ at equilibrium requires a large $[O_2]\ (g)$ and vice versa. In this case, the slope of the line

is equal to K.

d. According to figure 15.8, we could obtain a graph with the x-axis labeled $[O2]\ (M)$ and y-axis labeled $[SO2]\ (M)$. The graph should have a positive linear correlation. For every $3\ O_2\ (g)$ there is $2\ SO_2\ (g)$. Because the magnitudes of the two concentrations are directly proportional, a large $O_2\ (g)$ at equilibrium requires a large $SO_2\ (g)$ and vice versa. In this case, the slope of the line is equal to K.

2.

a.

$K = [Na_2CO_3][CO_2][H_2O]$

If $[CO_2]$ is doubled, $[H_2O]$ should be halved if the system is to maintain equilibrium.

b.

$K = \frac{[NF_2]^2}{[N_2F_4]}$

If $[NF_2]$ is decreased by a factor of 2, then $[N_2F_4]$ must also be decreased by a factor of 2 if the system is to maintain equilibrium.

c.

$K = \frac{[HI]^2}{[H_2][I_2]}$

If $[I_2]$ is doubled then $[HI]$ must also be doubled if the system is to maintain equilibrium.

3.

a.

$K = \frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}$

If $[CS_2]$ is doubled then $[H_2]$ must be decreased by a factor of 2√4≅ 1.189 if the system is to maintain equilibrium.

b.

$K = \frac{[PCl_3]}{[Cl_2][PCl_5]}$

If $[Cl_2]$ is halved then $[PCl_5]$ must also be halved if the system is to maintain equilibrium.

c.

$K = \frac{[NO]^4[H_2O]^6}{[NH_3][O_2]^5}$

If $[NO]$ is doubled then $[H_2O]$ must also be multiplied by 22/3≅1.587 if the system is to maintain equilibrium.

Numerical Problems

1. The data in the following table were collected at 450°C for the reaction $N_2\ (g) + 3\ H_2\ (g) \rightleftharpoons 2\ NH_3\ (g)$:

	Equilibrium Partial Pressure (atm)		
P (atm)	NH_3	N_2	H_2
30 (equilibrium)	1.740	6.588	21.58

P (atm)	Equilibrium Partial Pressure (atm)		
	NH_3	N_2	H_2
100	15.20	19.17	65.13
600	321.6	56.74	220.8

The reaction equilibrates at a pressure of 30 atm. The pressure on the system is first increased to 100 atm and then to 600 atm. Is the system at equilibrium at each of these higher pressures? If not, in which direction will the reaction proceed to reach equilibrium?

2. For the reaction $A \rightleftharpoons B + C$, K at 200°C is 2.0. A 6.00 L flask was used to carry out the reaction at this temperature. Given the experimental data in the following table, all at 200°C, when the data for each experiment were collected, was the reaction at equilibrium? If it was not at equilibrium, in which direction will the reaction proceed?

Experiment	A	B	C
1	2.50 M	2.50 M	2.50 M
2	1.30 atm	1.75 atm	14.15 atm
3	12.61 mol	18.72 mol	6.51 mol

3. The following two reactions are carried out at 823 K:

$$CoO\,(s) + H_2\,(g) \rightleftharpoons Co\,(s) + H_2O\,(g) \text{ with } K = 67 \tag{15.E.12}$$

$$CoO\,(s) + CO\,(g) \rightleftharpoons Co\,(s) + CO_2\,(g) \text{ with } K = 490 \tag{15.E.13}$$

   a. Write the equilibrium expression for each reaction.
   b. Calculate the partial pressure of both gaseous components at equilibrium in each reaction if a 1.00 L reaction vessel initially contains 0.316 mol of H_2 or CO plus 0.500 mol CoO.
   c. Using the information provided, calculate Kp for the following reaction:

$$H_2\,(g) + CO_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g) \tag{15.E.14}$$

   d. Describe the shape of the graphs of [reactants] versus [products] as the amount of CoO changes.

4. Hydrogen iodide (HI) is synthesized via $H_2\ (g) + I_2\ (g) \rightleftharpoons 2\ HI\ (g)$, for which $K_p = 54.5$ at 425°C. Given a 2.0 L vessel containing $1.12 \times 10^{-2}\ mol$ of H_2 and $1.8 \times 10^{-3}\ mol$ of I_2 at equilibrium, what is the concentration of HI? Excess hydrogen is added to the vessel so that the vessel now contains $3.64 \times 10^{-1}\ mol$ of H_2. Calculate Q and then predict the direction in which the reaction will proceed. What are the new equilibrium concentrations?

Answers

1. The system is not at equilibrium at each of these higher pressures. To reach equilibrium, the reaction will proceed to the right to decrease the pressure because the equilibrium partial pressure is less than the total pressure.

$$K_p = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[15.20]^2}{[19.17][65.13]^3} = 4.4 \times 10^{-5}$$

$$K_p = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[321.6]^2}{[56.74][220.8]^3} = 1.7 \times 10^{-4}$$

2.

1. $K = \frac{[B][C]}{[A]} = \frac{[2.50][2.50]}{[2.50]} = 2.50$

2. $K_p = K(RT)^{\Delta n} \rightarrow K = \frac{K_p}{(RT)^{\Delta n}} = \frac{19.0}{((0.08206\frac{L \cdot atm}{mol \cdot K})(200+273.15)K)^{2-1})} = 0.49$

$$K_p = \frac{(P_B)(P_C)}{(P_A)} = \frac{(1.75)(14.15)}{1.30} = 19.0$$

3. $K = \frac{[B][C]}{[A]^2} = \frac{(18.72)(6.51)}{12.61} = 9.7$

Experiment 1 is about the same as the given K value and thus considered to be about equilibrium. The second experiment has a K value that is about 1 so neither the formation of the reactants or products is favored. The third experiment has a K value that is larger than 1 so the formation of the products is favored.

3.

a.

$K = \frac{[H_2O]}{[H_2]}$

$K = \frac{[CO_2]}{[Co]}$

b.

$[H_2] = [CO] = 0.316\ mol\ H_2 \times \frac{1}{1.00\ L} = 0.316\ M$

$[CoO] = 0.5\ mol\ CoO \times \frac{1}{1.00\ L} = 0.5\ M$

Reaction 1:

$PV = nRT \rightarrow P = \frac{nRT}{V} = (4.65 \times 10^{-3})(0.08206\frac{L \cdot atm}{mol \cdot K})(823\ K) = 0.314$

$[H_2] = 0.316 - x = 0.316 - 0.311 = 4.65x10^{-3}$

$PV = nRT \rightarrow P = \frac{nRT}{V} = (0.311)(0.08206\frac{L \cdot atm}{mol \cdot K})(823\ K) = 21.0$

$[H_2O] = x = 0.311$

	H_2	H_2O
I	0.316	0
C	-x	+x
E	0.316-x	x

$K = \frac{[H_2O]}{[H_2]} \rightarrow 67 = \frac{x}{0.316-x} \rightarrow x = 0.311$

Reaction 2:

$PV = nRT \rightarrow P = \frac{nRT}{V} = (0.001)(0.08206\frac{L \cdot atm}{mol \cdot K})(823\ K) = 6.75 \times 10^{-2}\ atm$

$[CO] = 0.316 - x = 0.316 - 0.315 = 0.001\ M$

$PV = nRT \rightarrow P = \frac{nRT}{V} = (0.315)(0.08206\frac{L \cdot atm}{mol \cdot K})(823\ K) = 21.3\ atm$

$[CO_2] = x = 0.315\ M$

	CO	CO_2
I	0.316	0
C	-x	+x
E	0.316-x	x

$K = \frac{[CO_2]}{[Co]} \rightarrow 490 = \frac{x}{0.316-x} \rightarrow x = 0.315$

c.

$H_2\ (g) + CO_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g)$

$K_p = \frac{(P_{CO})(P_{H_2O})}{(P_{H_2})(P_{CO_2})} = \frac{(6.75\times10^{-2})(21)}{(0.314)(21.3)} = 0.21$

d. The shape of the graphs [reactants] versus [products] does not change as the amount of CoO changes because it is a solid.

4.

$PV = nRT \rightarrow \frac{n}{V} = \frac{P}{RT} \rightarrow \frac{n}{V} = \frac{0.101798}{(0.08206\frac{L\cdot atm}{mol\cdot K})((425+273.15)\ K)} = 1.5\times10^{-4}\ M\ HI$

$[HI] = 2x = 2(0.050899) = 0.101798\ atm$

$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} \rightarrow 54.5 = \frac{(2x)^2}{(3.2\times10^{-1}-x)(5.16\times10^{-2}-x)} \rightarrow x = 0.050899\ atm$

	H_2	I_2	HI
I	3.2×10^{-1}	5.16×10^{-2}	0
C	-x	-x	+2x
E	$3.2\times10^{-1}-x$	$5.16\times10^{-2}-x$	2x

$PV = nRT \rightarrow P = \frac{nRT}{V} = (5.6\times10^{-3})(0.08206\frac{L\cdot atm}{mol\cdot K})((425+273.15)\ K) = 3.2\times10^{-1}\ atm$

$[H_2] = 1.12\times10^{-2}\ mol\ H_2 \times \frac{1}{2.0\ L} = 5.6\times10^{-3}\ M$

$PV = nRT \rightarrow P = \frac{nRT}{V} = (9.0\times10^{-4})(0.08206\frac{L\cdot atm}{mol\cdot K})((425+273.15)\ K) = 5.16\times10^{-2}\ atm$

$[I_2] = 1.8\times10^{-3}\ mol\ I_2 \times \frac{1}{2.0\ L} = 9.0\times10^{-4}\ M$

For excess hydrogen:

$Q = \frac{[HI]}{[H_2][I_2]} = \frac{1.8\times10^{-3}}{(594.410)(1.09\times10^{-3})} = 2.8\times10^{-3}$

The reaction will proceed to the right to reach equilibrium.

$PV = nRT \rightarrow \frac{n}{V} = \frac{P}{RT} \rightarrow \frac{0.103162}{(0.08206\frac{L\cdot atm}{mol\cdot K})((425+273.15)\ K)} = 1.8\times10^{-3}\ M$

$[HI] = 2x = 2(0.051581) = 0.103162\ atm$

$PV = nRT \rightarrow \frac{n}{V} = \frac{P}{RT} \rightarrow \frac{10.375}{(0.08206\frac{L\cdot atm}{mol\cdot K})((425+273.15)\ K)} = 594.410\ M$

$[H_2] = 10.427 - x = 10.427 - 0.051581 = 10.375\ atm$

$PV = nRT \rightarrow \frac{n}{V} = \frac{P}{RT} \rightarrow \frac{1.9\times10^{-5}}{(0.08206\frac{L\cdot atm}{mol\cdot K})((425+273.15)\ K)} = 1.09\times10^{-3}\ M$

$[I_2] = 5.16\times10^{-2} - x = 5.16\times10^{-2} - 0.051581 = 1.9\times10^{-5}\ atm$

$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} \rightarrow 54.5 = \frac{(2x)^2}{(10.427-x)(5.16\times10^{-2}-x)} \rightarrow x = 0.051581\ atm$

	H_2	I_2	HI
I	10.427	5.16×10^{-2}	0
C	-x	-x	+2x
E	10.427-x	$5.16\times10^{-2}-x$	2x

$PV = nRT \rightarrow P = \frac{nRT}{V} = (0.182\ M)(0.08206\frac{L\cdot atm}{mol\cdot K})((425+273.15)\ K) = 10.427\ atm$

$$[H_2] = 3.64 \times 10^{-1}\ mol\ H_2 \times \frac{1}{2.0\ L} = 0.182\ M$$

15.7: Le Chatelier's Principle

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15.S: Chemical Equilibrium (Summary)

chemical equilibrium – condition where the concentration of products and reactants do not change with time

15.1: The Concept of Equilibrium

at equilibrium

$$k_f[A] = k_r[B]$$

there for the ratio

$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = constant$$

15.2: The Equilibrium Constant

equilibrium condition can be reached from either forward or reverse direction

Cato Maximillian Galdberg (1836-1902), and Peter Wauge (1833-1900)

- Law of mass action – relationship between concentrations of reactants and products at equilibrium

If $aA + bB \rightleftharpoons pP + qQ$

then an equilibrium expression can be constructed

$$K_c = \frac{[P]^p[Q]^q}{[A]^a[B]^b}$$

- equilibrium expression depends only on stoichiometry of reaction and not mechanisms
- equilibrium constant:
- does not depend on initial concentrations
- does not matter if other substances present as long as they do not react with reactants or products
- varies with temperatures
- no units

15.2.1 Expressing Equilibrium Constants in Terms of Pressure, K_p

$$K_p = \frac{(P_P)^p(P_Q)^q}{(P_A)^a(P_B)^b}$$

15.2.2 The Magnitude of Equilibrium Constants

- $K \gg 1$; equilibrium lies to the right; products favored
- $K \ll 1$; equilibrium lies to the left; reactants favored

15.2.3 The Direction of the Chemical Equation and K

- equilibrium expression written in one direction is the reciprocal of the one in the other direction

15.3: Interpreting & Working with Equilibrium Constants

15.4: Heterogeneous Equilibria

- homogeneous equilibria – substances in the same phase
- heterogeneous equilibria – substances in different phases
- a pure solid, a pure liquid, and a solvent in dilute solutions all appear in equilibrium laws, but they are all assigned activities that are equal to 1
- by convention the actvities of the pure solid, pure liquid, or solute are not explicitly written as part of the equilibrium law

15.5: Calculating Equilibrium Constants

determining unknown equilibrium concentrations

- tabulate known initial and equilibrium concentrations
- calculate change in concentration that occurs as system reaches equilibrium
- use stoichiometry to determine change in concentration of unknown species
- from initial concentrations and changes in concentrations, calculate equilibrium concentrations

15.5.1 Relating K_c and K_p

$$PV = nRT$$

\[P = (n/V)RT = MRT \nonumber \]

$$PA = [A](RT)$$

$$K_p = K_c(RT)D^n$$

- D n = change in moles from reactants to products

15.6: Applications of Equilibrium Constants

- equilibrium constant:
  1. product direction reaction mixture will proceed
  2. calculate concentrations of reactants and products once equilibrium is reached

15.6.1 Predicting the Direction of Reaction

- reaction quotient
- at equilibrium Q=K
- Q>K; reaction moves right to left
- Q

15.6.2 Calculating of Equilibrium Concentrations

15.7: Le Chatelier's Principle

If system at equilibrium is disturbed by change in temperature, pressure or concentration then system will shift equilibrium position

15.7.1 Change in Reactant or Product Concentration

- addition of substance will result in consummation of part of added substance
- if substance removed, reaction will move to produce more of the substance

15.7.2 Effects of Volume and Pressure Changes

- reducing volume, reaction shifts to reduce number of gas molecules
- increase volume, reaction shifts to produce more gas molecules
- increase pressure, decrease volume reduces total number of moles
- pressure volume changes do not affect K as long as temperature is constant
- changes concentrations of gaseous substances

15.7.3 Effect on Temperature Change

- endothermic: reactants + heat « products
- exothermic: reactants « products + heat
- increase temperature, equilibrium shifts in direction that absorbs heat
- endothermic: increase T, increase K
- exothermic: increase T, decrease K
- cooling shifts equilibrium to produce heat

15.7.4 The Effect of Catalysts

- catalysts increase rate at which equilibrium is obtained
- does not change composition of equilibrium mixture

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16: ACID–BASE EQUILIBRIA

Acids and bases have been defined differently by three sets of theories. One is the Arrhenius definition, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. On the other hand, the Bronsted-Lowry definition defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons. Also, the Lewis theory of acids and bases states that acids are electron pair acceptors while bases are electron pair donors. Acids and bases can be defined by their physical and chemical observations.

16.1: Acids and Bases - A Brief Review

16.2: Brønsted–Lowry Acids and Bases

16.3: The Autoionization of Water

16.4: The pH Scale

16.5: Strong Acids and Bases

16.6: Weak Acids

16.7: Weak Bases

16.8: Relationship Between Ka and Kb

16.9: Acid-Base Properties of Salt Solutions

16.10: Acid-Base Behavior and Chemical Structure

16.11: Lewis Acids and Bases

16.E: Acid–Base Equilibria (Exercises)

16.S: Acid–Base Equilibria (Summary)

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16.1: Acids and Bases - A Brief Review

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Acids and bases are common solutions that exist everywhere. Almost every liquid that we encounter in our daily lives consists of acidic and basic properties, with the exception of water. They have completely different properties and are able to neutralize to form H_2O, which will be discussed later in a subsection. Acids and bases can be defined by their physical and chemical observations (Table 16.1.1).

Table 16.1.1: General Properties of Acids and Bases

ACIDS	BASES
produce a piercing pain in a wound.	give a slippery feel.
taste sour.	taste bitter.
are colorless when placed in phenolphthalein (an indicator).	are pink when placed in phenolphthalein (an indicator).
are red on blue litmus paper (a pH indicator).	are blue on red litmus paper (a pH indicator).
have a pH<7.	have a pH>7.
produce hydrogen gas when reacted with metals.	
produce carbon dioxide when reacted with carbonates.	
Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are **electrolytes**. Strong acids and bases will be strong electrolytes. Weak acids and bases will be weak electrolytes. This affects the amount of conductivity.

The Arrhenius Definition of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

An Arrhenius acid is a compound that increases the concentration of H^+ ions that are present when added to water. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

In this reaction, hydrochloric acid (HCl) dissociates into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby

releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure H_2SO_4 or HCl dissolved in toluene are not acidic, despite the fact that both of these acids will donate a proton to toluene. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment.

Limitation of the Arrhenius Definition of Acids and Bases

The Arrhenius definition can **only** describe acids and bases in an aqueous environment.

In chemistry, acids and bases have been defined differently by three sets of theories: One is the Arrhenius definition defined above, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. The other two definitions are discussed in detail alter in the chapter and include the Brønsted-Lowry definition the defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons and the Lewis theory of acids and bases states that acids are electron pair acceptors while bases are electron pair donors.

Contributors and Attributions

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16.2: Brønsted–Lowry Acids and Bases

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Previously, we defined acids and bases as Arrhenius did: An acid is a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited. We extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ^1_1H, loses an electron. A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{16.2.1}$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{16.2.2}$$

$$HF \rightleftharpoons H^+ + F^- \tag{16.2.3}$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{16.2.4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{16.2.5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{16.2.6}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{16.2.7}$$

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{16.2.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{16.2.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{16.2.10}$$

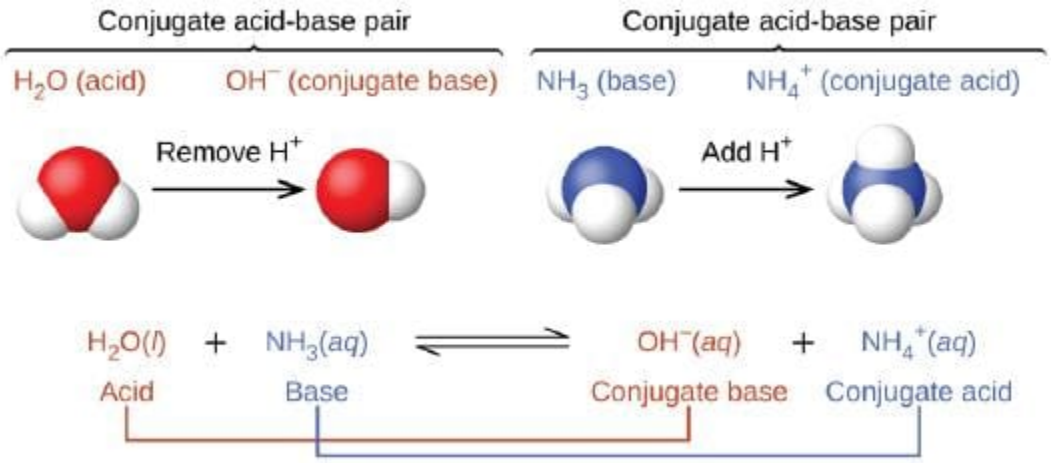
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{16.2.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{16.2.12}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{16.2.13}$$

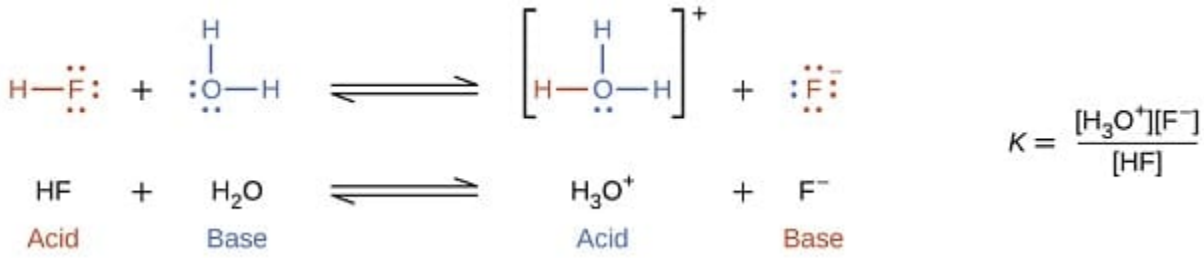
\[\ce{F^- +H^+ \rightleftharpoons HF} \label{16.2.3g} \]

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



A conjugate acid base pair if when we remove a H plus from the acid to get the conjugate base. Another conjugate acid base pair is when we add H plus to a base to get a conjugate acid. In a reaction: the acid and base are the reactants and the products are the conjugate base and conjugate acid.

The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:

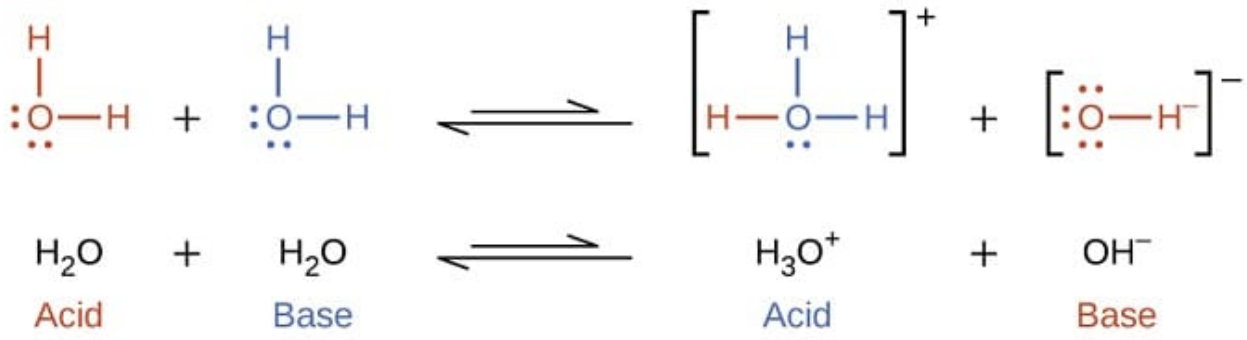


In this reaction HF is treated as the acid and water is treated as the base. The products as H3O plus and F minus. H3O plus is the acid and F minus is the base.

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:

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Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



Here we have 2 water molecules reacting together. One water molecule is an acid while the second water molecule acts as a base. For the products, we get H3O plus and OH minus. H3O plus is the acid and OH minus is the base.

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$\mathrm{H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + HO^-{}_{(aq)} \quad K_w = [H_3O^+][OH^-]} \tag{16.2.14}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.

YouTube Video

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A Video Discussing Conjugate Acid-Base Pairs: Conjugate Acid-Base Pairs [youtu.be]

Example 16.2.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^{2+} = [OH^-]^{2+} = 1.0 \times 10^{-14}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal 1.0×10^{-7} M.

Exercise 16.2.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium determined by the autoionization reaction but it does shift the relative concentrations of $[OH^-]$ and $[H_3O^+]$. Example 16.2.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

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A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw) [youtu.be]

Example 16.2.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 16.2.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons [redacted]_{3(aq)} + H_3O^+_{(aq)} \quad (16.2.15)$$

$$HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-_{(aq)} \quad (16.2.16)$$

Example 16.2.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

a. as an acid with OH^-
b. as a base with HI

Solution

a. $HSO^-_{3(aq)} + OH^-_{(aq)} \rightleftharpoons SO^{2-}_{3(aq)} + H_2O_{(l)}$
b. $HSO^-_{3(aq)} + HI_{(aq)} \rightleftharpoons H_2SO_{3(aq)} + I^-_{(aq)}$

Example 16.2.4

Write separate equations representing the reaction of $H_2PO_4^-$

a. as a base with HBr
b. as an acid with OH^-

Answer

a. $H_2PO^-_{4(aq)} + HBr_{(aq)} \rightleftharpoons H_3PO_{4(aq)} + Br^-_{(aq)}$
b. $H_2PO^-_{4(aq)} + OH^-_{(aq)} \rightleftharpoons HPO^{2-}_{4(aq)} + H_2O_{(l)}$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the

base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_2O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C$$

Key Equations

- $$K_w = [H_3O^+][OH^-\,] = 1.0 \times 10^{-14} \text{ (at 25 °C)}$$

Glossary

acid ionization
: reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
: species that may either gain or lose a proton in a reaction

amphoteric
: species that can act as either an acid or a base

autoionization
: reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
: reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
: proton donor

Brønsted-Lowry base
: proton acceptor

conjugate acid
: substance formed when a base gains a proton

conjugate base
: substance formed when an acid loses a proton

ion-product constant for water (K_w)
: equilibrium constant for the autoionization of water

Contributors and Attributions

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16.3: The Autoionization of Water

Learning Objectives

- To understand the autoionization reaction of liquid water.
- To know the relationship among pH, pOH, and pK_w.

As you learned previously acids and bases can be defined in several different ways (Table 16.3.1). Recall that the Arrhenius definition of an acid is a substance that dissociates in water to produce H^+ ions (protons), and an Arrhenius base is a substance that dissociates in water to produce OH^- (hydroxide) ions. According to this view, an acid–base reaction involves the reaction of a proton with a hydroxide ion to form water. Although Brønsted and Lowry defined an acid similarly to Arrhenius by describing an acid as any substance that can donate a proton, the Brønsted–Lowry definition of a base is much more general than the Arrhenius definition. In Brønsted–Lowry terms, a base is any substance that can accept a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton. Consequently, all Brønsted–Lowry acid–base reactions actually involve two conjugate acid–base pairs and the transfer of a proton from one substance (the acid) to another (the base). In contrast, the Lewis definition of acids and bases, focuses on accepting or donating pairs of electrons rather than protons. A Lewis base is an electron-pair donor, and a Lewis acid is an electron-pair acceptor.

Table 16.3.1: Definitions of Acids and Bases

Definition	Acids	Bases
Arrhenius	H^+ donor	OH^- donor
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

Because this chapter deals with acid–base equilibria in aqueous solution, our discussion will use primarily the Brønsted–Lowry definitions and nomenclature. Remember, however, that all three definitions are just different ways of looking at the same kind of reaction: a proton is an acid, and the hydroxide ion is a base—no matter which definition you use. In practice, chemists tend to use whichever definition is most helpful to make a particular point or understand a given system. If, for example, we refer to a base as having one or more lone pairs of electrons that can accept a proton, we are simply combining the Lewis and Brønsted–Lowry definitions to emphasize the characteristic properties of a base.

Acid–Base Properties of Water

Recall that because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions (Cl^-) and protons (H^+). The proton, in turn, reacts with a water molecule to form the hydronium ion (H_3O^+):

$$\underset{acid}{HCl_{(aq)}} + \underset{base}{H_2O_{(l)}} \rightarrow \underset{acid}{H_3O^+_{(aq)}} + \underset{base}{Cl^-_{(aq)}} \tag{16.3.1}$$

In this reaction, HCl is the acid, and water acts as a base by accepting an H^+ ion. The reaction in Equation 16.3.1 is often written in a simpler form by removing H_2O from each side:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \tag{16.3.2}$$

In Equation 16.3.2, the hydronium ion is represented by H^+, although free H^+ ions do not exist in liquid water as this reaction demonstrates:

$$H^+_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)}$$

Water can also act as an acid, as shown in Equation 16.3.3. In this equilibrium reaction, H_2O donates a proton to NH_3, which acts as a base:

$$\underset{acid}{H_2O_{(l)}} + \underset{base}{NH_{3(aq)}} \rightleftharpoons \underset{acid}{NH^+_{4(aq)}} + \underset{base}{OH^-_{(aq)}} \tag{16.3.3}$$

Water is thus termed amphiprotic, meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that Equation 16.3.3 is an equilibrium reaction as indicated by the double arrow and hence has an equilibrium constant associated with it.

The Ion-Product Constant of Liquid Water

Because water is amphiprotic, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an autoionization process:

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{16.3.4}$$

The equilibrium constant K for this reaction can be written as follows:

$$K_a = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a^2_{H_2O}} \approx \frac{[H_3O^+][HO^-]}{(1)^2} = [H_3O^+][HO^-] \tag{16.3.5}$$

where a is the activity of a species. Because water is the solvent, and the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. The activity of each solute is approximated by the molarity of the solute.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that Ka = $K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation Ka = $K_{eq}(a_{H_2O}$). Because a_{H_2O} = 1 for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

In this reaction, one water molecule acts as an acid and one water molecule acts as a base. Thus, this reaction actually can be designated as the K_a of water and as the K_b of water. It is most common, however, to designate this reaction and the associated law of mass action as the K_w of water:

$$K_w = [H_3O^+][HO^-] \tag{16.3.6}$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25 °C, the concentrations of the hydronium ion and the hydroxide ion are equal:

$$[H_3O^+] = [OH^-] = 1.003 \times 10^{-7}\ M \tag{16.3.7}$$

Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb.

Substituting the values for $[H_3O^+]$ and $[OH^-]$ at 25 °C into this expression

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14} \tag{16.3.8}$$

Thus, to three significant figures, $K_w = 1.01 \times 10^{-14}$ *at room temperature,* and

$$K_w = 1.01 \times 10^{-14} = [H_3O^+][OH^-] \tag{16.3.9}$$

.

Like any other equilibrium constant, K_w varies with temperature, ranging from 1.15×10^{-15} at 0 °C to 4.99×10^{-13} at 100 °C.

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral.

If $[H_3O^+] > [OH^-]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^-]$, the solution is basic. For an aqueous solution, the H_3O^+ concentration is a quantitative measure of acidity: the higher the H_3O^+ concentration, the more acidic the solution. Conversely, the higher the OH^- concentration, the more basic the solution. In most situations that you will encounter, the H_3O^+ and OH^- concentrations from the dissociation of water are so small ($1.003 \times 10^{-7} M$) that they can be ignored in calculating the H_3O^+ or OH^- concentrations of solutions of acids and bases, but this is not always the case.

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A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw): [youtu.be]

The Relationship among pH, pOH, and pK_w

The pH scale is a concise way of describing the H_3O^+ concentration and hence the acidity or basicity of a solution. Recall that pH and the H^+ (H_3O^+) concentration are related as follows:

$$pH = -\log_{10}[H^+] \tag{16.3.10}$$

$$[H^+] = 10^{-pH} \tag{16.3.11}$$

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of 10 in their hydronium ion concentrations. Recall also that the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7}\ M$), whereas acidic solutions have pH < 7.00 (corresponding to $[H_3O^+] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[H_3O^+] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous pOH scale to describe the hydroxide ion concentration of a solution. The pOH and $[OH^-]$ are related as follows:

$$pOH = -\log_{10}[OH^-] \tag{16.3.12}$$

$$[OH^-] = 10^{-pOH} \tag{16.3.13}$$

The constant K_w can also be expressed using this notation, where $pK_w = -\log\ K_w$.

Because a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25 °C is 7.00 + 7.00 = 14.00. We can show that the sum of pH and pOH is equal to 14.00 for any aqueous solution at 25 °C by taking the negative logarithm of both sides of Equation ???:

$$-\log_{10} K_w = pK_w \tag{16.3.14}$$

$$= -\log([H_3O^+][OH^-]) \tag{16.3.15}$$

$$= (-\log[H_3O^+]) + (-\log[OH^-]) \tag{16.3.16}$$

$$= pH + pOH \tag{16.3.17}$$

Thus at any temperature, $pH + pOH = pK_w$, so at 25 °C, where $K_w = 1.0 \times 10^{-14}$, pH + pOH = 14.00. More generally, the pH of any neutral solution is half of the pK_w at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in Figure 16.3.1 over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

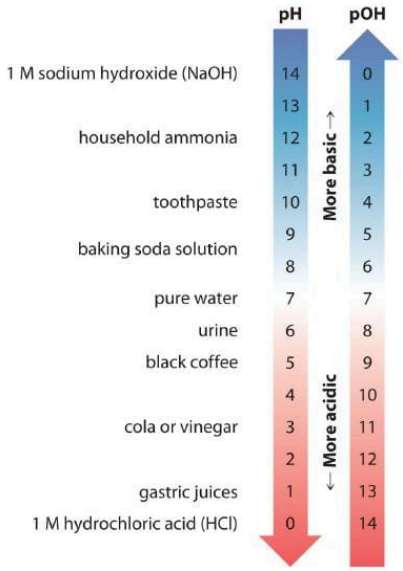


Figure 16.3.1: The Inverse Relationship between the pH and pOH Scales. As pH decreases, $[H^+]$ and the acidity increase. As pOH increases, $[OH^-]$ and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic.
Zero is the most acidic and fourteen is the most basic on the pH scale. Zero is the most basic and fourteen is the most acidic on the pOH scale.

For any neutral solution, pH + pOH = 14.00 (at 25 °C) with pH=pOH=7.

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A Video Introduction to pH: Introduction to pH [youtu.be]

Example 16.3.1

The K_w for water at 100 °C is 4.99×10^{-13}. Calculate pK_w for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100 °C. Report pH and pOH values to two decimal places.

Given: K_w

Asked for: pK_w, pH, and pOH

Strategy:

A. Calculate pK_w by taking the negative logarithm of K_w.
B. For a neutral aqueous solution, $[H_3O^+] = [OH^-]$. Use this relationship and Equation 16.3.9 to calculate $[H_3O^+]$ and $[OH^-]$. Then determine the pH and the pOH for the solution.

Solution:

A

Because pK_w is the negative logarithm of Kw, we can write

$$pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$$

The answer is reasonable: K_w is between 10^{-13} and 10^{-12}, so pK_w must be between 12 and 13.

B

Equation ??? shows that $K_w = [H_3O^+][OH^-]$. Because $[H_3O^+] = [OH^-]$ in a neutral solution, we can let $x = [H_3O^+] = [OH^-]$:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= (x)(x) = x^2 \\ x &= \sqrt{K_w} \\ &= \sqrt{4.99 \times 10^{-13}} \\ &= 7.06 \times 10^{-7}\ M \end{aligned}$$

Because x is equal to both $[H_3O^+]$ and $[OH^-]$,

$$\begin{aligned} pH = pOH &= -\log(7.06 \times 10^{-7}) \\ &= 6.15\ \text{(to two decimal places)} \end{aligned}$$

We could obtain the same answer more easily (without using logarithms) by using the pK_w. In this case, we know that $pK_w = 12.302$, and from Equation 16.3.17, we know that $pK_w = pH + pOH$. Because $pH = pOH$ in a neutral solution, we can use Equation 16.3.17 directly, setting $pH = pOH = y$. Solving to two decimal places we obtain the following:

$$\begin{aligned} pK_w &= pH + pOH \\ &= y + y \\ &= 2y \\ y &= \frac{pK_w}{2} \\ &= \frac{12.302}{2} \\ &= 6.15 = pH = pOH \end{aligned}$$

Exercise 16.3.1

Humans maintain an internal temperature of about 37 °C. At this temperature, $K_w = 3.55 \times 10^{-14}$. Calculate pK_w and the pH and the pOH of a neutral solution at 37 °C. Report pH and pOH values to two decimal places.

Answer available at the end of this section.

Summary

Water is amphiprotic: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion (H_3O^+). The autoionization of liquid water produces OH^- and H_3O^+ ions. The equilibrium constant for this reaction is called the ion-product constant of liquid water (Kw) and is defined as $K_w = [H_3O^+][OH^-]$. At 25 °C, K_w is 1.01×10^{-14}; hence $pH + pOH = pK_w = 14.00$.

- For any neutral solution, $pH + pOH = 14.00$ (at 25 °C) and $pH = 1/2pK_w$.
- Ion-product constant of liquid water:

$$K_w = [H_3O^+][OH^-]$$

- Definition of pH:

$$pH = -\log 10[H^+]$$

or

$$[H^+] = 10^{-pH}$$

- Definition of pOH:

$$pOH = -\log_{10}[OH^+]$$

or

$$[OH^-] = 10^{-pOH}$$

- Relationship among pH, pOH, and pK_w:

$$pK_w = pH + pOH$$

Answers

Exercise 16.3.1

- $pK_w = 13.45$
- $pH = pOH = 6.73$

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16.4: The pH Scale

Learning Objectives

- To define the pH scale as a measure of acidity of a solution

Because of its *amphoteric* nature (i.e., acts as both an acid or a base), water does not always remain as H_2O molecules. In fact, two water molecules react to form hydronium and hydroxide ions:

$$2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq) \tag{16.4.1}$$

This is also called the self-ionization of water. The concentration of H_3O^+ and OH^- are equal in pure water because of the 1:1 stoichiometric ratio of Equation 1. The molarity of H_3O^+ and OH^- in water are also both $1.0 \times 10^{-7}\ M$ at 25° C. Therefore, a constant of water (K_w) is created to show the equilibrium condition for the self-ionization of water. The product of the molarity of hydronium and hydroxide ion is always 1.0×10^{-14}.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{16.4.2}$$

This equations also applies to all aqueous solutions. However, K_w does change at different temperatures, which affects the pH range discussed below.

H^+ and H_3O^+ is often used interchangeably to represent the hydrated proton, commonly call the hydronium ion.

The equation for water equilibrium is:

$$H_2O \rightleftharpoons H^+ + OH^- \tag{16.4.3}$$

- If an acid (H^+) is added to the water, the equilibrium shifts to the left and the OH^- ion concentration decreases
- If base (OH^-) is added to water, the equilibrium shifts to left and the H^+ concentration decreases.

pH and pOH

The constant of water determines the range of the pH scale. To understand what the pK_w is, it is important to understand first what the "p" means in pOH, and pH. The Danish biochemist Søren Sørenson proposed the term pH to refer to the "potential of hydrogen ion." He defined the "p" as the negative of the logarithm, -log, of $[H^+]$. Therefore the pH is the negative logarithm of the molarity of H. The pOH is the negative logarithm of the molarity of OH^- and the pK_w is the negative logarithm of the constant of water. These definitions give the following equations:

$$pH = -\log[H^+] \tag{16.4.4}$$

$$pOH = -\log[OH^-] \tag{16.4.5}$$

$$pK_w = -\log[K_w] \tag{16.4.6}$$

At room temperature (25 °C),

$$K_w = 1.0 \times 10^{-14} \tag{16.4.7}$$

So

$$pK_w = -\log[1.0 \times 10^{-14}] \tag{16.4.8}$$

Using the properties of logarithms, Equation 16.4.8 can be rewritten as

$$10^{-pK_w} = 10^{-14}. \tag{16.4.9}$$

By substituting, we see that pK_w is 14. The equation also shows that each increasing unit on the scale decreases by the factor of ten on the concentration of H^+. For example, a pH of 1 has a molarity ten times more concentrated than a solution of pH 2.

Since

$$pK_w = 14 \tag{16.4.10}$$

$$pK_w = pH + pOH = 14 \tag{16.4.11}$$

Definitions

- A solution with more OH^- ions than H^+ ion is **basic;** for aqueous solutions at 25°C that corresponds to pH > 7.
- A solution with more H^+ ions than OH^- ions is **acidic;** for aqueous solutions at 25°C that corresponds to pH < 7.
- A solution with that same concentration of H^+ ions than OH^- ions is **neutral;** for aqueous solutions at 25°C that corresponds to pH = 7.

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(4.9 \times 10^{-7}) = 6.31 \tag{16.4.12}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(4.9 \times 10^{-7}) = 6.31 \tag{16.4.13}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 16.4.1).

> The pH scale is logarithmic, meaning that an increase or decrease of an integer value changes the concentration by a tenfold. For example, a pH of 3 is ten times more acidic than a pH of 4. Likewise, a pH of 3 is one hundred times more acidic than a pH of 5. Similarly a pH of 11 is ten times more basic than a pH of 10.

Figure 16.4.1 depicts the pH scale with common solutions and where they are on the scale.

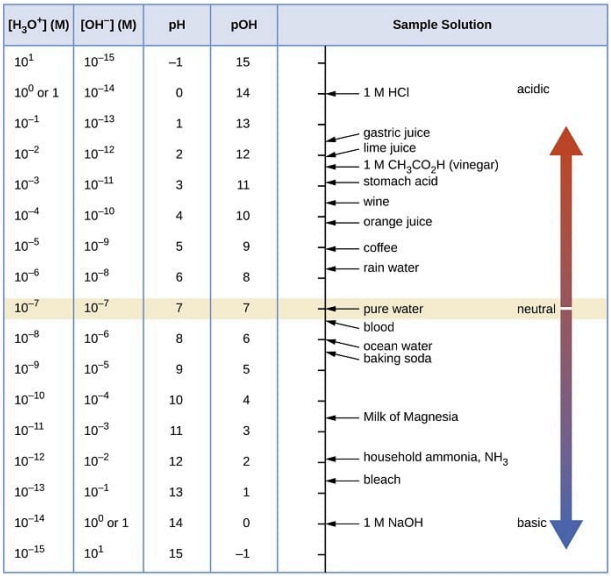


Figure 16.4.1: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart. Image used with permisison (CC -BY; OpenStax)

The pH scale does not have upper nor lower bounds!

It is common that the pH scale is argued to range from 0-14 or perhaps 1-14, but neither is correct. The pH range does not have an upper nor lower bound, since as defined above, the pH is an indication of concentration of H^+. For example, at a pH of zero the hydronium ion concentration is one molar, while at pH 14 the hydroxide ion concentration is one molar. Typically the concentrations of H^+ in water in most solutions fall between a range of 1 M (pH=0) and 10^{-14} M (pH=14). Hence a range of 0 to 14 provides sensible (but not absolute) "bookends" for the scale. One can go somewhat below zero and somewhat above 14 in water, because the concentrations of hydronium ions or hydroxide ions can exceed one molar.

Example 16.4.1

If the concentration of $NaOH$ in a solution is $2.5 \times 10^{-4}\ M$, what is the concentration of H_3O^+?

Solution

Because

$$1.0 \times 10^{-14} = [H_3O^+][OH^-]$$

to find the concentration of H_3O^+, solve for the $[H_3O^+]$.

$$\frac{1.0 \times 10^{-14}}{[OH^-]} = [H_3O^+]$$

$$\frac{1.0 \times 10^{-14}}{2.5 \times 10^{-4}} = [H_3O^+] = 4.0 \times 10^{-11}\ M$$

Example 16.4.2

a. Find the pH of a solution of 0.002 M of HCl.
b. Find the pH of a solution of 0.00005 M NaOH.

Solution

a. The equation for pH is -log [H+]

$$[H^+] = 2.0 \times 10^{-3}\ M$$

$$pH = -\log[2.0 \times 10^{-3}] = 2.70$$

b. The equation for pOH is -log [OH^-]

$$[OH^-] = 5.0 \times 10^{-5}\ M$$

$$pOH = -\log[5.0 \times 10^{-5}] = 4.30$$

$$pK_w = pH + pOH$$

and

$$pH = pK_w - pOH$$

then

$$pH = 14 - 4.30 = 9.70$$

Example 16.4.3: Soil

If moist soil has a pH of 7.84, what is the H^+ concentration of the soil solution?

Solution

$$pH = -\log[H^+]$$

$$7.84 = -\log[H^+]$$

$$[H^+] = 1.45 \times 10^{-8} M$$

Hint: Place -7.84 in your calculator and take the antilog (often inverse log or 10^x) = 1.45 x 10^{-8}M

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Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\mathrm{pH} = -\log \mathrm{H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathrm{pOH} = -\log[\mathrm{OH^-}]$. In pure water, pH = 7.00 and pOH = 7.00.

References

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2. Segel, Irwin H. "Acid and Base." *Biochemical Calculations*. 2nd ed. Wiley: BK Book, 1976. 12.
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16.5: Strong Acids and Bases

Learning Objectives

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- To understand the leveling effect.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A– is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{16.5.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{16.5.2}$$

As we noted earlier, because water is the solvent, it has an activity equal to 1, so the $[H_2O]$ term in Equation 16.5.2 is actually the a_{H_2O}, which is equal to 1.

Again, for simplicity, H_3O^+ can be written as H^+ in Equation 16.5.3.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \tag{16.5.3}$$

Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form hydronium ions, H_3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them unitless. The values of K_a for a number of common acids are given in Table 16.5.1.

Table 16.5.1: *Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)*

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^9	–9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^2	–2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^1	–1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
***The number in parentheses indicates the ionization step referred to for a polyprotic acid.**						

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0
***The number in parentheses indicates the ionization step referred to for a polyprotic acid.**						

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{16.5.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{16.5.5}$$

Once again, the activity of water has a value of 1, so water does not appear in the equilibrium constant expression. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 16.5.2.

Table 16.5.2: Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH+)

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0*	0.00
***As in Table 16.5.1.**						

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{16.5.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{16.5.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{16.5.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{16.5.9}$$

If we add Equations 16.5.6 and 16.5.7, we obtain the following:

add Equations 16.5.6 and 16.5.7, we obtain

Reaction	Equilibrium Constants
$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}}$	$K_a = [H^+]\,\cancel{[CN^-]} \,/\, \cancel{[HCN]}$
$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}}$	$K_b = [OH^-]\,\cancel{[HCN]} \,/\, \cancel{[CN^-]}$
$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$	$K = K_a \times K_b = [H^+][OH^-]$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_aK_b = K_w \tag{16.5.10}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{16.5.11}$$

$$K_a = 10^{-pK_a} \tag{16.5.12}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{16.5.13}$$

$$K_b = 10^{-pK_b} \tag{16.5.14}$$

Similarly, Equation 16.5.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{16.5.15}$$

At 25 °C, this becomes

$$pK_a + pK_b = 14.00 \tag{16.5.16}$$

The values of pK_a and pK_b are given for several common acids and bases in Tables 16.5.1 and 16.5.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a million times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

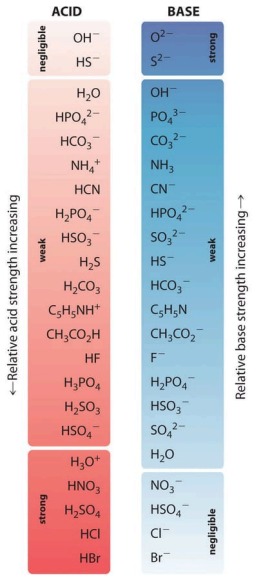


Figure 16.5.1: The Relative Strengths of Some Common Conjugate Acid–Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Strong acids are H3O plus, HNO3, H2SO4, HCl, and HBr. Negligible acids are HS minus and OH minus. Stron bases are O negative 2, S negative 2. Negligible bases are NO3 minus, HSO4 minus, Cl minus, and Br minus.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 16.5.1. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 16.5.2 are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

The conjugate base of a strong acid is a weak base and vice versa.

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{16.5.17}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3CO_2{}_{(aq)}^-}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.

Example 16.5.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 16.5.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equations 16.5.15 and 16.5.16. Use the relationships pK = –log K and $K = 10^{-pK}$ (Equations 16.5.11 and 16.5.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 16.5.16: $pK_a + pK_b = pK_w = 14.00$. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 16.5.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

Because pK_a = –log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27$$

$$pKa + pK_b = 14.00$$

$$pK_a = 10.73$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

Exercise 16.5.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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A Video Calculating pH in Strong Acid or Strong Base Solutions: Calculating pH in Strong Acid or Strong Base Solutions [youtu.be]

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table $16.5.1$ that acids like H_2SO_4 and HNO_3 lie above the hydronium ion, meaning that they have pK_a values less than zero and are stronger acids than the H_3O^+ ion. Recall from Chapter 4 that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving HNO_3 instead. In fact, all six of the common strong acids that we first encountered in Chapter 4 have pK_a values less than zero, which means that they have a greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 108 greater than K_a for HNO_3, the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I– or NO_3^-. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, regardless of the identity of the strong acid. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O. Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like a weak acid in this solvent. This result clearly tells us that HI is a stronger acid than HNO_3. The relative order of acid strengths and approximate K_a and pK_a values for the strong acids at the top of Table $16.5.1$ were determined using measurements like this and different nonaqueous solvents.

> In *aqueous solutions*, H_3O^+ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O.

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH– is leveled to the strength of OH– because OH– is the strongest base that can exist in equilibrium with water. Salts such as K_2O, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table $16.5.2$, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + 2K^+_{(aq)} \tag{16.5.18}$$

$$NaOCH_{3(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + CH_3OH_{(aq)} \tag{16.5.19}$$

$$NaNH_{2(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + NH_{3(aq)} \tag{16.5.20}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).

Polyprotic Acids and Bases

As you learned, polyprotic acids such as H_2SO_4, H_3PO_4, and H_2CO_3 contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases. Consider H_2SO_4, for example:

$$HSO^-_{4(aq)} \rightleftharpoons SO^{2-}_{4(aq)} + H^+_{(aq)} \quad pK_a = -2$$

The equilibrium in the first reaction lies far to the right, consistent with H_2SO_4 being a strong acid. In contrast, in the second reaction, appreciable quantities of both HSO_4^- and SO_4^{2-} are present at equilibrium.

> For a polyprotic acid, acid strength decreases and the pK_a increases with the sequential loss of each proton.

The hydrogen sulfate ion (HSO_4^-) is both the conjugate base of H_2SO_4 and the conjugate acid of SO_4^{2-}. Just like water, HSO4– can therefore act as either an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion (SO_4^{2-}) is a polyprotic base that is capable of accepting two protons in a stepwise manner:

$$SO^{2-}_{4(aq)} + H_2O_{(aq)} \rightleftharpoons HSO^-_{4(aq)} + OH^-_{(aq)}$$

$$HSO^-_{4(aq)} + H_2O_{(aq)} \rightleftharpoons H_2SO_{4(aq)} + OH^-_{(aq)} \tag{16.5.21}$$

Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by pK_a + pK_b = pKw. Consider, for example, the HSO_4^-/SO_4^{2-} conjugate acid–base pair. From Table 16.5.1, we see that the pK_a of HSO_4^- is 1.99. Hence the pK_b of SO_4^{2-} is 14.00 − 1.99 = 12.01. Thus sulfate is a rather weak base, whereas OH^- is a strong base, so the equilibrium shown in Equation 16.5.21 lies to the left. The HSO_4^- ion is also a very weak base (pK_a of H_2SO_4 = 2.0, pK_b of $HSO_4^- = 14 - (-2.0) = 16$), which is consistent with what we expect for the conjugate base of a strong acid.

Example 16.5.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $NH^+_{4(aq)} + PO^{3-}_{4(aq)} \rightleftharpoons NH_{3(aq)} + HPO^{2-}_{4(aq)}$
- $CH_3CH_2CO_2H_{(aq)} + CN^-_{(aq)} \rightleftharpoons CH_3CH_2CO^-_{2(aq)} + HCN_{(aq)}$

Given: balanced chemical equation

Asked for: equilibrium position

Strategy:

Identify the conjugate acid–base pairs in each reaction. Then refer to Tables 16.5.1and16.5.2 and Figure 16.5.2 to determine which is the stronger acid and base. Equilibrium **always** favors the formation of the weaker acid–base pair.

Solution:

The conjugate acid–base pairs are NH_4^+/NH_3 and HPO_4^{2-}/PO_4^{3-}. According to Tables 16.5.1 and 16.5.2, NH_4^+ is a stronger acid ($pK_a = 9.25$) than HPO_4^{2-} (pKa = 12.32), and PO_4^{3-} is a stronger base ($pK_b = 1.68$) than NH_3 ($pK_b = 4.75$). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{NH^+_{4(aq)}} + \underset{\text{stronger base}}{PO^{3-}_{4(aq)}} \rightleftharpoons \underset{\text{weaker base}}{NH_{3(aq)}} + \underset{\text{weaker acid}}{HPO^{2-}_{4(aq)}}$$

The conjugate acid–base pairs are $CH_3CH_2CO_2H/CH_3CH_2CO_2^-$ and HCN/CN^-. According to Table 16.5.1, HCN is a weak acid (pKa = 9.21) and CN^- is a moderately weak base (pKb = 4.79). Propionic acid ($CH_3CH_2CO_2H$) is not listed in Table 16.5.1, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties are listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the

carboxylic acid ($-CH_2CH_3$ versus $-CH_3$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the pK_a of propionic acid to be similar in magnitude to the pK_a of acetic acid. (In fact, the pK_a of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{CH_3CH_2CO_2H_{(aq)}} + \underset{\text{stronger base}}{CN^-_{(aq)}} \rightleftharpoons \underset{\text{weaker base}}{CH_3CH_2CO^-_{2(aq)}} + \underset{\text{weaker acid}}{HCN_{(aq)}}$$

Exercise 16.5.1

Predict whether the equilibrium for each reaction lies to the left or the right as written.

a. $H_2O_{(l)} + HS^-_{(aq)} \rightleftharpoons OH^-_{(aq)} + H_2S_{(aq)}$
b. $HCO^-_{2(aq)} + HSO^-_{4(aq)} \rightleftharpoons HCO_2H_{(aq)} + SO^{2-}_{4(aq)}$

Answer a available at the end of this section.

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A Video Discussing Polyprotic Acids: Polyprotic Acids [youtu.be]

Summary

Acid–base reactions always contain two conjugate acid–base pairs. Each acid and each base has an associated ionization constant that corresponds to its acid or base strength. Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (K_a). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (K_b). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the leveling effect. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_a K_b = K_w$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a$$
$$K_a = 10^{-pK_a}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b$$
$$K_b = 10^{-pK_b}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w$$
$$pK_a + pK_b = 14.00 \text{ at } 25°\text{C}$$

Contributors and Attributions

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Answers

Exercise 16.5.1**: Lactic Acid**

- $K_a = 1.4 \times 10^{-4}$ for lactic acid;
- pK_b = 10.14 and
- $K_b = 7.2 \times 10^{-11}$ for the lactate ion

Exercise 16.5.1

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16.6: Weak Acids

Learning Objectives

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure $16.6.1$ lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure $16.6.1$*: Some of the common strong acids and bases are listed here.*

Six Strong Acids		Six Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

we write the equation for the ionization constant as:

$$K_\mathrm{a} = \frac{[H3O+][A-]}{[HA]}$$

where the concentrations are those at equilibrium. As noted in the section on equilibrium constants, although water is a reactant in the reaction, it is the solvent as well, so its activity has a value of 1, which does not change the value of K_a.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_a = K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_a = K_{eq}(a_{H_2O})$. Because $a_{H_2O} = 1$ for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

he larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- relative o the concentration of the nonionized acid, HA. Thus a stronger acid has a larger onization constant than does a weaker acid. The ionization constants increase as ne strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength: $CH_3CO_2H < HNO_2 < HSO_4^-$

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$
$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2{}^-(aq) \qquad K_a = 4.6 \times 10^{-4}$$
$$HSO_4{}^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4{}^{2-}(aq) \qquad K_a = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\% \text{ ionization} = \frac{[H3O+]_{eq}}{[HA]_0} \times 100\% \tag{16.6.1}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 16.6.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H3O+]_{eq}}{[HNO2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2{}^-(aq) + H_3O^+(aq).$$

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 16.6.1) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 16.6.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer available at the end of this section.

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base

of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 16.6.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq),$$

we write the equation for the ionization constant as:

$$K_\mathrm{b} = \frac{[HB+][OH-]}{[B]}$$

where the concentrations are those at equilibrium. Again, we do not see water in the equation because water is the solvent and has an activity of 1. The chemical reactions and ionization constants of the three bases shown are:

$$\mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 2.17 \times 10^{-11}$$
$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 5.6 \times 10^{-10}$$
$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 1.8 \times 10^{-5}$$

A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $\mathrm{HA} - \mathrm{A^-}$:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

with $K_\mathrm{a} = \frac{[H3O+][A-]}{[HA]}$.

$$\mathrm{A^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{HA}(aq)$$

with $K_\mathrm{b} = \frac{[HA][OH]}{[A-]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\mathrm{HA}(aq)} + \mathrm{H_2O}(l) + \cancel{\mathrm{A^-}(aq)} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \cancel{\mathrm{A^-}(aq)} + \mathrm{OH^-}(aq) + \cancel{\mathrm{HA}(aq)}$$
$$2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_\mathrm{a} \times K_\mathrm{b} = \frac{[H3O+][A-]}{[HA]} \times \frac{[HA][OH-]}{[A-]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_\mathrm{w}$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_\mathrm{a} \times K_\mathrm{b} = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_\mathrm{w}$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger

conjugate bases (Figure 16.6.2).

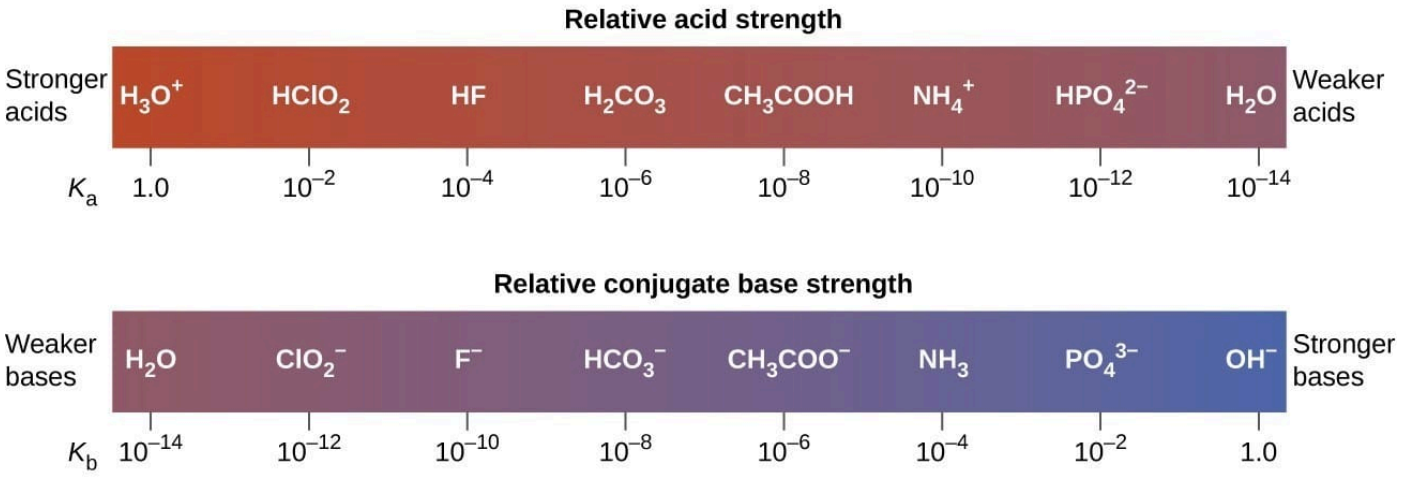


Figure 16.6.2: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 16.6.3 lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure 16.6.3 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 16.6.3 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 16.6.3 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

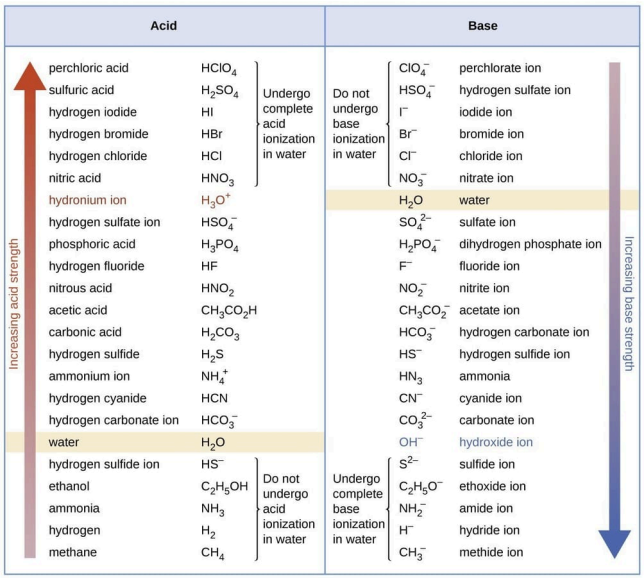


Figure 16.6.3: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 16.6.3. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that

lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Example 16.6.2: The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$\begin{aligned} K_a &= \frac{K_w}{K_b} \\ &= \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} \\ &= 4.6 \times 10^{-4} \end{aligned}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

Exercise 16.6.2

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 as 4.9×10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Answer available at the end of this section.

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid (CH_3CO_2H) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 16.6.4). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]} = 1.8 \times 10^{-5}$$

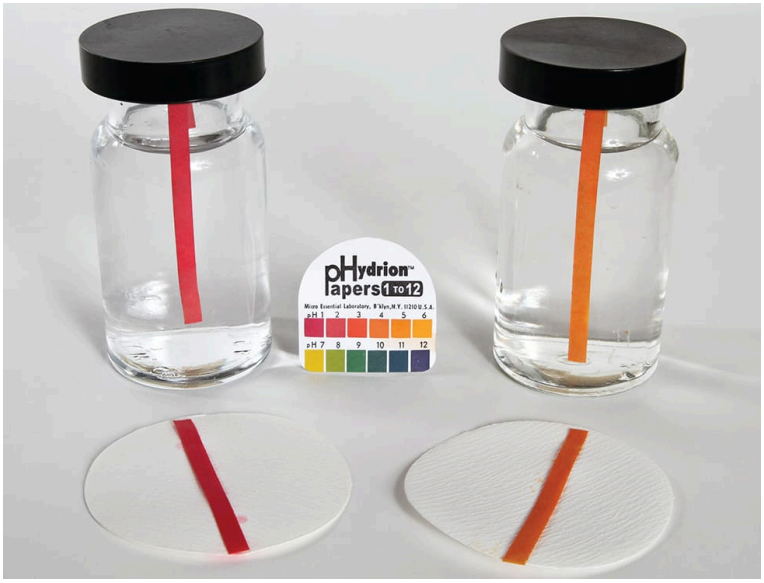


Figure 16.6.4: pH paper indicates that a 0.1-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+]$ = 0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 ($[H_3O^+]$ = 0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa)

This image shows two bottles containing clear colorless solutions. Each bottle contains a single p H indicator strip. The strip in the bottle on the left is red, and a similar red strip is placed on a filter paper circle in front of the bottle on surface on which the bottles are resting. Similarly, the second bottle on the right contains and orange strip and an orange strip is placed in front of it on a filter paper circle. Between the two bottles is a pack of p Hydrion papers with a p H color scale on its cover.

Table 16.6.1: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table 16.6.1 gives the ionization constants for several weak acids; additional ionization constants can be found in Table E1.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$$

This gives an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 14.4.5). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the **ionization constant** of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_{\mathrm{b}} = \frac{[(CH3)3NH+][OH-]}{[(CH3)3N]}$$



Figure 16.6.5: pH paper indicates that a 0.1-M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-]$ = 0.001 M) because the weak base NH_3 only partially reacts with water. A 0.1-M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base (credit: modification of work by Sahar Atwa).

The ionization constants of several weak bases are given in Table 16.6.2 and Table E2.

Table 16.6.2: Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25 °C
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6N_5NH_3^+ + OH^-$	4.3×10^{-10}

Example 16.6.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 *M* and $[H_3O^+] = [CH_3CO_2^-] = 0.00118\ M$. What is the value of K_a for acetic acid?



Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

$$K_\mathrm{a} = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]}$$

$$= \frac{(0.00118)(0.00118)}{0.0787}$$

$$= 1.77 \times 10^{-5}$$

Exercise 16.6.3

What is the equilibrium constant for the ionization of the $\mathrm{HSO_4^-}$ ion, the weak acid used in some household cleansers:

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[\mathrm{H_3O^+}] = 0.027\ M$; $[\mathrm{HSO_4^-}] = 0.29\ M$; and $[\mathrm{SO_4^{2-}}] = 0.13\ M$.

Answer available at the end of this section.

Example 16.6.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2] = 0.050\ M$, $[\mathrm{C_8H_{10}N_4O_2H^+}] = 5.0 \times 10^{-3}\ M$, and $[OH^-] = 2.5 \times 10^{-3}\ M$?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$\mathrm{C_8H_{10}N_4O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}(aq) + \mathrm{OH^-}(aq)$$

so

$$K_b = \frac{[C8H10N4O2H+][OH-]}{[C8H10N4O2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Exercise 16.6.4

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^{-}(aq) + OH^{-}(aq)$$

In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium with:

- $[OH^-] = 1.3 \times 10^{-6} M$
- $[H_2PO_4^-]$=0.042 M and
- $[HPO_4^{2-}]$=0.341 M.

Answer available at the end of this section.

Example 16.6.5: Determination of K_a or K_b from pH

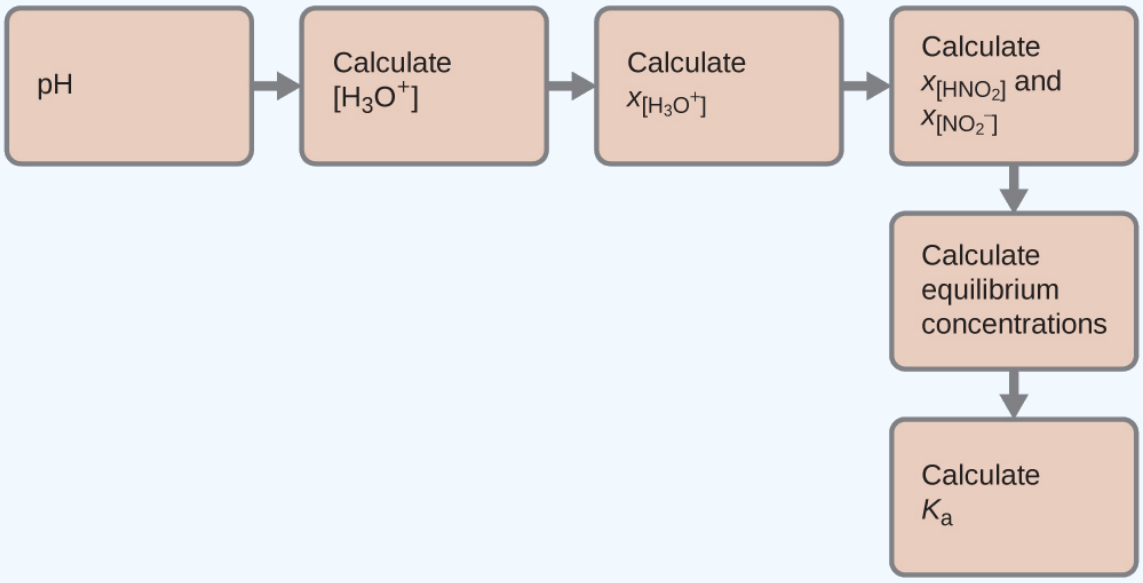
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here. Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction.

	HNO_2 + H_2O ⇌ H_3O^+ + NO_2^-			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	x	x
Equilibrium concentration (*M*)	$[HNO_2]_i + (-x) = 0.0516 + (-x)$		$[H_3O]^+ + x[NO_2]^- + x$ ~0 + x	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The change in concentration of H_3O^+, $x_{[H_3O^+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 + H_2O ⇌ H_3O^+ + NO_2^-			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	$x = 0.0046$	$x = 0.0046$
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H3O+][NO2-]}{[HNO2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 16.6.5

The pH of a solution of household ammonia, a 0.950-*M* solution of NH_3, is 11.612. What is K_b for NH_3.

Answer available at the end of this section.

Example 16.6.6: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq) \quad K_\mathrm{a} = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq)$$

Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction so we do not need to consider it when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.534 + (-x)$	$0 + x = x$	$0 + x = x$

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_a = 1.8 \times 10^{-4} = \frac{[H3O+][HCO2-]}{[HCO2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$x^2 = 0.534 \times (1.8 \times 10^{-4})$$

$$= 9.6 \times 10^{-5}$$

$$x = \sqrt{9.6 \times 10^{-5}}$$

$$= 9.8 \times 10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534}$$

$$= 1.8 \times 10^{-2} \, (1.8$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$[\mathrm{H_3O^+}] = \ 0 + x = 0 + 9.8 \times 10^{-3} \, M.$$

$$= 9.8 \times 10^{-3} \, M$$

The pH of the solution can be found by taking the negative log of the $[\mathrm{H_3O^+}]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

Exercise 16.6.6: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \quad K_a = 1.8 \times 10^{-5}$$

Hint available at the end of this section.

Answer available at the end of this section.

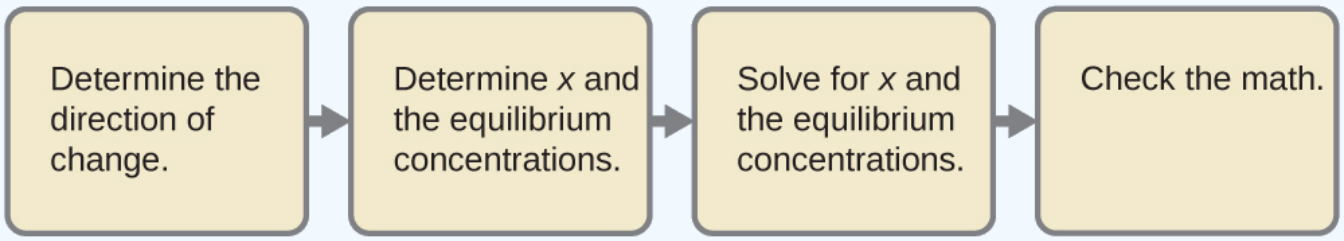
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

Example 16.6.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-*M* solution of trimethylamine, a weak base:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \quad K_b = 6.3 \times 10^{-5}$$

Solution This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 16.6.6. The reactants and products will be different and the numbers will be different, but the logic will be the same:



1. Determine x and equilibrium concentrations. The table shows the changes and concentrations:

	$(CH_3)_3N$ + H_2O ⇌ $(CH_3)_3NH^+$ + OH^-			
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	−*x*		*x*	*x*
Equilibrium concentration (*M*)	0.25 + (−*x*)		0 + *x*	~0 + *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_b = \frac{[(CH3)3NH+][OH-]}{[(CH3)3N]} = \frac{(x)(x)}{0.25 - x =} 6.3 \times 10^{-5}$$

If we assume that *x* is small relative to 0.25, then we can replace (0.25 – *x*) in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$([OH^-] = \ 0 + x = x = 4.0 \times 10^{-3}\ M$$
$$= 4.0 \times 10^{-3}\ M$$

Then calculate pOH as follows:

$$pOH = -\log(4.3 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$pH + pOH = pK_w = 14.00$$

permits the computation of pH:

$$pH = 14.00 - pOH = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

Exercise 16.6.7

a. Show that the calculation in Step 2 of this example gives an *x* of 4.3 × 10^{-3} and the calculation in Step 3 shows K_b = 6.3 × 10^{-5}.
b. Find the concentration of hydroxide ion in a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76 × 10^{-5}. Calculate the percent ionization of ammonia, the fraction ionized × 100, or $\frac{[NH4+]}{[NH3]} \times 100\%$

Answer a available at the end of this section.

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that *x* is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

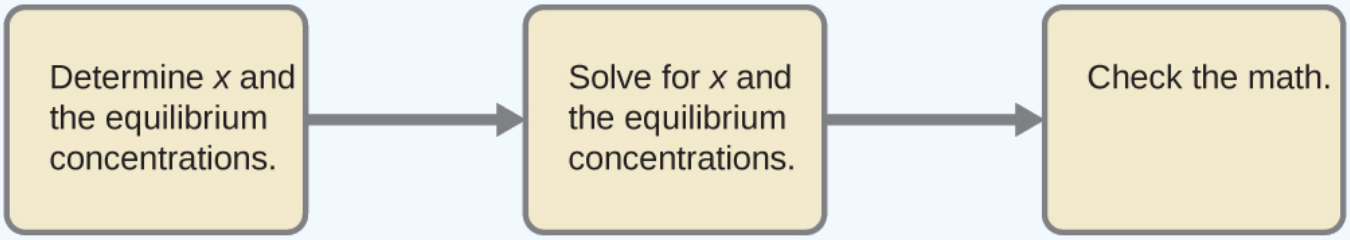
Example 16.6.8: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^- + H_2O ⇌ H_3O^+ + SO_4^{2-}			
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	−*x*		*x*	*x*
Equilibrium concentration (*M*)	0.50 + (−*x*) = 0.50 − *x*)		0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H3O+][SO4^{2}-]}{[HSO4-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that *x* is small and approximate (0.50 – *x*) as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[\mathrm{HSO_4^-}]_i} \overset{?}{\leq} 0.05$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^{2+}$$

or

$$x^{2+} + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^{2+} - 4ac}}{2a}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$\begin{aligned}[\mathrm{H_3O^+}] = \ & 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ & = 7.2 \times 10^{-2}\ M\end{aligned}$$

The pH of this solution is:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 7.2 \times 10^{-2} = 1.14$$

Exercise 16.6.8

a. Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.
b. Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+(aq) + \text{OH}^-(aq) \quad K_\text{b} = 2.5 \times 10^{-4}$$

Hint available at the end of this section.

Answer available at the end of this section.

The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order $\text{HCl} < \text{HBr} < \text{HI}$, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-}, and the amide ion, NH_2^-, are such strong bases that they react completely with water:

$$[redacted](aq) + \text{H}_2\text{O}(l) \longrightarrow \text{OH}^-(aq) + \text{OH}^-(aq)$$

$$\text{NH}_2^-(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{NH}_3(aq) + \text{OH}^-(aq)$$

Thus, O^{2-} and NH_2^- appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$. Likewise, for group 16, the order of increasing acid strength is $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$. Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$; across the third row, it is $\text{SiH}_4 < \text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$ (see Figure 16.6.6).

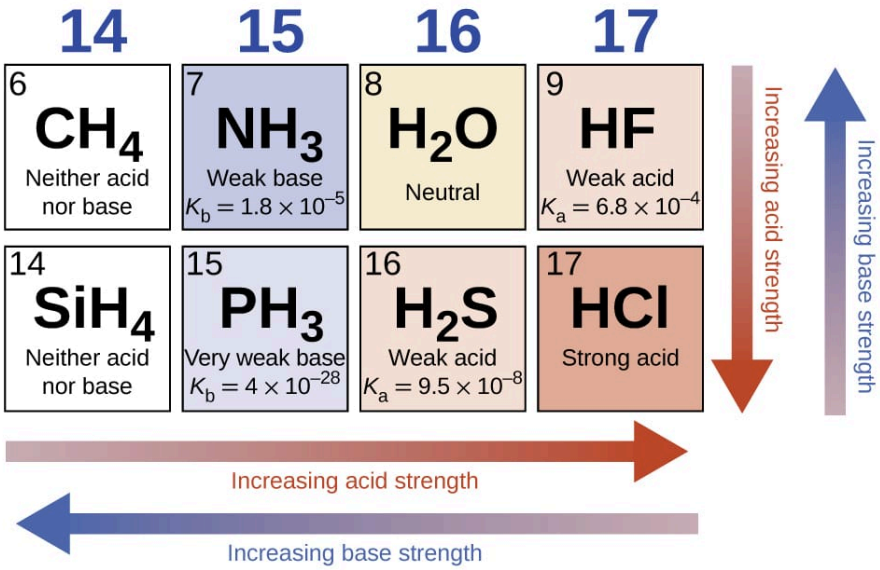
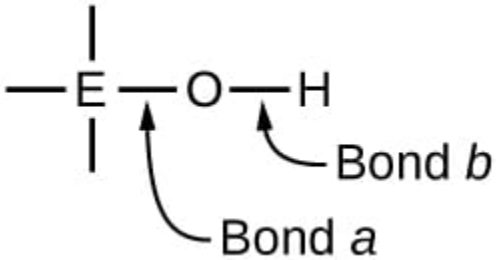


Figure 16.6.6: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

This diagram has two rows and four columns. Red arrows point left across the bottom of the figure and down at the right side and are labeled “Increasing acid strength.” Blue arrows point left across the bottom and up at the right side of the figure and are labeled “Increasing base strength.” The first column is labeled 14 at the top and two white squares are beneath it. The first has the number 6 in the upper left corner and the formula C H subscript 4 in the center along with designation Neither acid nor base. The second square contains the number 14 in the upper left corner, the formula C H subscript 4 at the center and the designation Neither acid nor base. The second column is labeled 15 at the top and two blue squares are beneath it. The first has the number 7 in the upper left corner and the formula N H subscript 3 in the center along with the designation Weak base and K subscript b equals 1.8 times 10 superscript negative 5. The second square contains the number 15 in the upper left corner, the formula P H subscript 3 at the center and the designation Very weak base and K subscript b equals 4 times 10 superscript negative 28. The third column is labeled 16 at the top and two squares are beneath it. The first is shaded tan and has the number 8 in the upper left corner and the formula H subscript 2 O in the center along with the designation neutral. The second square is shaded pink, contains the number 16 in the upper left corner, the formula H subscript 2 S at the center and the designation Weak acid and K subscript a equals 9.5 times 10 superscript negative 8. The fourth column is labeled 17 at the top and two squares are beneath it. The first is shaded pink, has the number 9 in the upper left corner and the formula H F in the center along with the designation Weak acid and K subscript a equals 6.8 times 10 superscript negative 4. The second square is shaded a deeper pink, contains the number 17 in the upper left corner, the formula H C l at the center, and the designation Strong acid.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



A diagram is shown that includes a central atom designated with the letter E. Single bonds extend above, below, left, and right of the E. An O atom is bonded to the right of the E, and an arrow points to the bond labeling it, “Bond a.” An H atom is single bonded to the right of the O atom. An arrow pointing to this bond connects it to the label, “Bond b.”

If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic –OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 16.6.7).

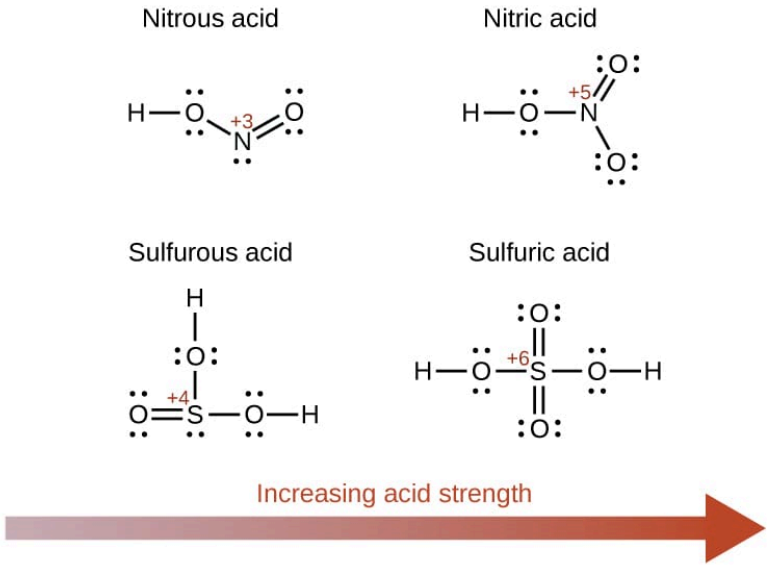


Figure 16.6.7: As the oxidation number of the central atom E increases, the acidity also increases.

A diagram is shown that includes four structural formulas for acids. A red, right pointing arrow is placed beneath the structures which is labeled “Increasing acid strength.” At the top left, the structure of Nitrous acid is provided. It includes an H atom to which an O atom with two unshared electron pairs is connected with a single bond to the right. A single bond extends to the right and slightly below to a N atom with one unshared electron pair. A double bond extends up and to the right from this N atom to an O atom which has two unshared electron pairs. To the upper right is a structure for Nitric acid. This structure differs from the previous structure in that the N atom is directly to the right of the first O atom and a second O atom with three unshared electron pairs is connected with a single bond below and to the right of the N atom which has no unshared electron pairs. At the lower left, an O atom with two unshared electron pairs is double bonded to its right to an S atom with a single unshared electron pair. An O atom with two unshared electron pairs is bonded above and an H atom is single bonded to this O atom. To the right of the S atom is a single bond to another O atom with two unshared electron pairs to which an H atom is single bonded. This structure is labeled “Sulfurous acid.” A similar structure which is labeled “Sulfuric acid” is placed in the lower right region of the figure. This structure differs in that an H atom is single bonded to the left of the first O atom, leaving it with two unshared electron pairs and a fourth O atom with two unshared electron pairs is double bonded beneath the S atom, leaving it with no unshared electron pairs.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]^-$, by reaction with hydroxide ion:

$$[Al(H_2O)_3(OH)_3](aq)+OH^-(aq) \rightleftharpoons H_2O(l) + [Al(H_2O)_2(OH)_4]^-(aq)$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $[Al(H_2O)_6]^{3+}$ by reaction with hydronium ion:

$$3\,H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_6{}^{3+}(aq) + 3\,H_2O(l)$$

In this case, protons are transferred from hydronium ions in solution to $\mathrm{Al(H_2O)_3(OH)_3}$, and the compound functions as a base.

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table (CH_4 < NH_3 < H_2O < HF), and they increase down a group (HF < HCl < HBr < HI). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases (H_2SO_3 < H_2SO_4). The strengths of oxyacids also increase as the electronegativity of the central element increases [H_2SeO_4 < H_2SO_4].

Key Equations

- $K_{\mathrm{a}} = \dfrac{[H3O+][A-]}{[HA]}$
- $K_{\mathrm{b}} = \dfrac{[HB+][OH-]}{[B]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \text{ (at room temperature)}$
- $\text{Percent ionization} = \dfrac{[H3O+]_{eq}}{[HA]_0} \times 100$

Glossary

acid ionization constant (K_a)
: equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)
: equilibrium constant for the ionization of a weak base

leveling effect of water
: any acid stronger than $\mathrm{H_3O^+}$, or any base stronger than OH^- will react with water to form $\mathrm{H_3O^+}$, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

oxyacid
: compound containing a nonmetal and one or more hydroxyl groups

percent ionization
: ratio of the concentration of the ionized acid to the initial acid concentration, times 100

Answers

Exercise 16.6.1

1.3% ionized

Exercise 16.6.2

$\mathrm{NH_4^+}$ is the slightly stronger acid (K_a for $\mathrm{NH_4^+}$ = 5.6 × 10^{-10}).

Exercise 16.6.3

K_a for $\mathrm{HSO_4^-} = 1.2 \times \times 10^{-2}$

Exercise 16.6.4

K_b for $\mathrm{HPO_4^{2-}} = 1.6 \times 10^{-7}$

Exercise 16.6.5

$K_b = 1.8 \times 10^{-5}$

Exercise 16.6.6**: acetic acid**

Determine $[\mathrm{CH_3CO_2^-}]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[CH3CO2-]}{[CH3CO2H]_{initial}} \times 100$.

Exercise $16.6.6$**: acetic acid**

percent ionization = 1.3%

Exercise $16.6.7$

$7.56 \times 10^{-4}\ M$, 2.33%

2.33%

Exercise $16.6.8$

It will be necessary to convert [OH^-] to $[\mathrm{H_3O^+}]$ or pOH to pH toward the end of the calculation.

Exercise $16.6.8$

pH 11.16

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16.7: Weak Bases

The pH of a solution of a weak base can be calculated in a way which is very similar to that used for a weak acid. Instead of an acid constant K_a, a base constant K_b must be used. If a weak base B accepts protons from water according to the equation

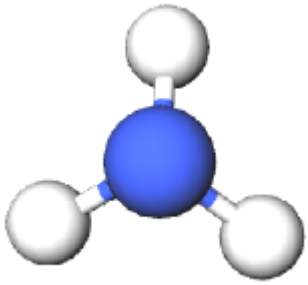
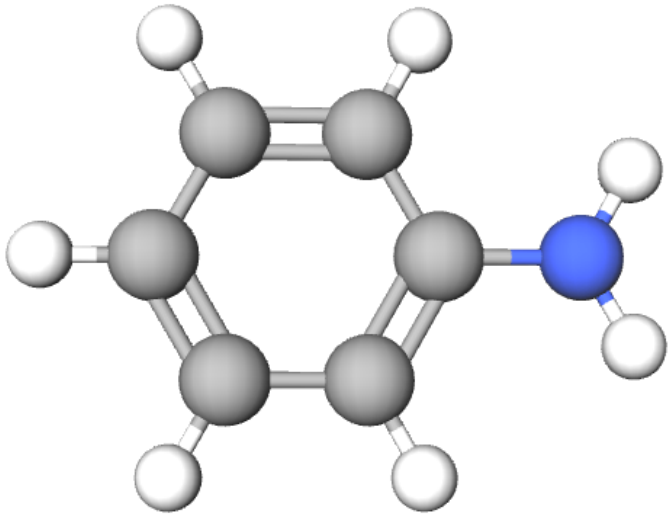
$$\mathrm{B} + \mathrm{H_2O} \rightleftharpoons \mathrm{BH^+} + \mathrm{OH^-} \tag{16.7.1}$$

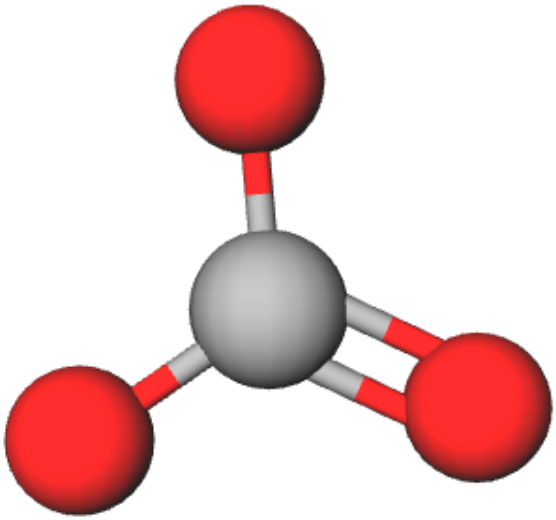
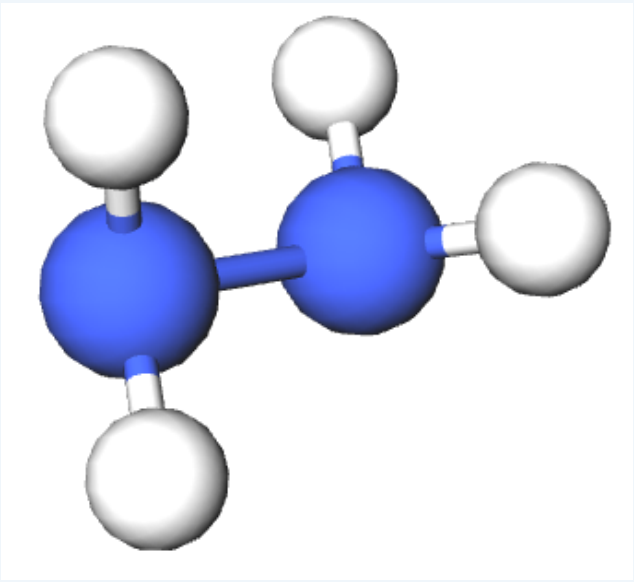
then the base constant is defined by the expression

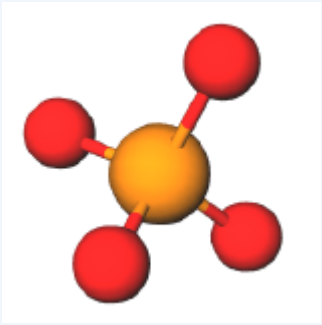
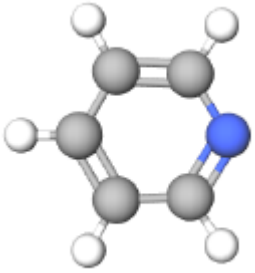
$$K_b = \frac{\mathrm{BH^+}\ \mathrm{OH^-}}{\mathrm{B}} \tag{16.7.2}$$

A list of K_b values for selected bases arranged in order of strength is given in the table below. This table is part of our larger collection of acid-base resources.

Table 16.7.1: The Base Constants for Some Bases at 25°C. Taken from Hogfelt, E. Perrin, D. D. Stability Constants of Metal Ion Complexes, 1st ed. Oxford; New Pergamon, 1979-1982. International Union of Pure and Applied Chemistry, Commission on Equilibrium. ISBN: 0080209580

Base	Formula and Ionization Equation	K_b	Molecular Shape
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.77×10^{-5}	
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	3.9×10^{-10}	

Base	Formula and Ionization Equation	K_b	Molecular Shape
Carbonate ion	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	2.1×10^{-4}	
Hydrazine	$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$ $N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^-$	$K_1 = 1.2 \times 10^{-6}$ $K_2 = 1.3 \times 10^{-15}$	
Hydride ion	$H^- + H_2O \rightarrow H_2 + OH^-$	1.0	

Base	Formula and Ionization Equation	K_b	Molecular Shape
Phosphate ion	$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$	5.9×10^{-3}	
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.6×10^{-9}	

To find the pH we follow the same general procedure as in the case of a weak acid. If the stoichiometric concentration of the base is indicated by c_b, the result is entirely analogous to equation 4 in the section on the pH of weak acids; namely,

$$K_b = \frac{[\mathrm{OH^-}]^2}{c_b - [\mathrm{OH^-}]} \tag{16.7.3}$$

Under most circumstances we can make the approximation

$$c_b - [OH^-] \approx c_b$$

in which case Equation 16.7.3 reduces to the approximation

$$[OH^-] \approx \sqrt{K_b c_b} \tag{16.7.4}$$

which is identical to the expression obtained in the acid case (approximation shown in equation 6 in the section on the pH of weak acids) except that OH^- replaces H_3O^+ and *b* replaces *a*. Once we have found the hydroxide-ion concentration from this approximation, we can then easily find the pOH, and from it the pH.

Example 16.7.1: pH using K_b

Using the value for K_b listed in the table, find the pH of 0.100 *M* NH_3.

Solution

It is not a bad idea to guess an approximate pH before embarking on the calculation. Since we have a dilute solution of a weak base, we expect the solution to be only mildly basic. A pH of 13 or 14 would be too basic, while a pH of 8 or 9 is too close to neutral. A pH of 10 or 11 seems reasonable. Using Equation 16.7.4 we have

$$
\begin{aligned}
[\ \mathrm{OH^-}] &= \sqrt{K_b c_b} \\
&= \sqrt{1.8\ \times\ 10^{-5}\ \mathrm{mol\ L^{-1}} \times\ 0.100\ \mathrm{mol\ L^{-1}}} \\
&= \sqrt{1.8\ \times\ 10^{-6}\ \mathrm{mol^2\ L^{-2}}} \\
&= 1.34\ \times\ 10^{-3}\ \mathrm{mol\ L^{-1}}
\end{aligned}
$$

Checking the accuracy of the approximation, we find

$$
\frac{[\ \mathrm{OH^-}]}{c_\mathrm{b}} = \frac{1.34\ \times\ 10^{-3}}{0.1} \approx 1\ \mathrm{percent}
$$

The approximation is valid, and we thus proceed to find the pOH.

$$
\mathrm{pOH} = -\log\frac{[\ \mathrm{OH^-}]}{\mathrm{mol\ L^{-1}}} = -\log(1.34\ \times\ 10^{-3}) = 2.87
$$

From which

$$
pH = 14.00–pOH = 14.00–2.87 = 11.13
$$

This calculated value checks well with our initial guess.

Occasionally we will find that the approximation

$$
c_b–[OH^-] \approx c_b
$$

is not valid, in which case we must use a series of successive approximations similar to that outlined above for acids. The appropriate formula can be derived from Equation 16.7.3 and reads

$$
[OH^-] \approx \sqrt{K_b(c_b - [OH^-])}
$$

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16.8: Relationship Between Ka and Kb

Learning Objectives

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A– is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{16.8.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[HA]} \tag{16.8.2}$$

The equilibrium constant for this reaction is the acid ionization constant K_a, also called the acid dissociation constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{16.8.3}$$

Thus the numerical values of K and K_a differ by the concentration of water (55.3 M). Again, for simplicity, H_3O^+ can be written as H^+ in Equation 16.8.3. Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form H^3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them **unitless**. The values of K_a for a number of common acids are given in Table 16.8.1.

Table 16.8.1: Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^9	–9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^2	–2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^1	–1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
***The number in parentheses indicates the ionization step referred to for a polyprotic acid.**						

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0
***The number in parentheses indicates the ionization step referred to for a polyprotic acid.**						

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{16.8.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{16.8.5}$$

Once again, the concentration does not appear in the equilibrium constant expression.. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 16.8.2.

Table 16.8.2*: Values of* K_b*,* pK_b*,* K_a*, and* pK_a *for Selected Weak Bases (B) and Their Conjugate Acids (BH+)*

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0*	0.00
***As in Table** 16.8.1**.**						

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{16.8.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{16.8.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{16.8.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{16.8.9}$$

If we add Equations 16.8.6 and 16.8.7, we obtain the following (recall that the equilibrium constant for the sum of two reactions is

the product of the equilibrium constants for the individual reactions):

$$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}} \quad K_a = [H^+]\,\cancel{[CN^-]} \,/\, \cancel{[HCN]} \tag{16.8.10}$$

$$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}} \quad K_b = [OH^-]\,\cancel{[HCN]} \,/\, \cancel{[CN^-]} \tag{16.8.11}$$

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \quad K = K_a \times K_b = [H^+][OH^-] \tag{16.8.12}$$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_aK_b = K_w \tag{16.8.13}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{16.8.14}$$

$$K_a = 10^{-pK_a} \tag{16.8.15}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{16.8.16}$$

$$K_b = 10^{-pK_b} \tag{16.8.17}$$

Similarly, Equation 16.5.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{16.8.18}$$

At 25°C, this becomes

$$pK_a + pK_b = 14.00 \tag{16.8.19}$$

The values of pK_a and pK_b are given for several common acids and bases in Table 16.5.1 and Table 16.5.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a 1000 times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 16.5. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 16.5.2 are the common strong acids; at the top right are the most common strong bases. **Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.**

> The conjugate base of a strong acid is a weak base and vice versa.

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base} \tag{16.8.20}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+

and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow\rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{16.8.21}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3CO_{2(aq)}{}^-} \tag{16.8.22}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)} \tag{16.8.23}$$

All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.

Example 16.8.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO^-_2$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH^+_2$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 16.5.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equation 16.5.15 and Equation 16.5.16. Use the relationships pK = –log K and K = 10–pK (Equation 16.5.11 and Equation 16.5.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 16.5.16: pK_a + pK_b = pKw = 14.00. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00 \tag{16.8.24}$$

$$pK_b = 14.00 - 4.83 = 9.17 \tag{16.8.25}$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 16.5.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14} \tag{16.8.26}$$

$$K_a = 1.9 \times 10^{-11} \tag{16.8.27}$$

Because pK_a = –log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27 \tag{16.8.28}$$

$$pKa + pK_b = 14.00 \tag{16.8.29}$$

$$pK_a = 10.73 \tag{16.8.30}$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11} \tag{16.8.31}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

Exercise 16.8.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer available at the end of this section.

Summary

Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (Ka). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (Kb). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair.

Key Takeaways

- The Ka and Kb values for a conjugated acid–base pairs are related through the K_w value:

$$K_aK_b = K_w \tag{16.8.32}$$

- The conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{16.8.33}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{16.8.34}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w \tag{16.8.35}$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a$$
$$K_a = 10^{-pK_a} \tag{16.8.36}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b$$
$$K_b = 10^{-pK_b} \tag{16.8.37}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w \tag{16.8.38}$$

$$pK_a + pK_b = 14.00 \text{ at } 25°\text{C} \tag{16.8.39}$$

Contributors and Attributions

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Answers

$K_a = 1.4 \times 10^{-4}$ for lactic acid;
pK_b = 10.14 and $K_b = 7.2 \times 10^{-11}$ for the lactate ion

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16.9: Acid-Base Properties of Salt Solutions

Learning Objectives

- To recognize salts that will produce acidic, basic, or neutral solutions in water
- To understand the Lewis acidity of small, highly-charged metal ions in water

A neutralization reaction can be defined as the reaction of an acid and a base to produce a salt and water. That is, another cation, such as Na^+, replaces the proton on the acid. An example is the reaction of CH_3CO_2H, a weak acid, with $NaOH$, a strong base:

$$\underset{acid}{CH_3CO_2H_{(l)}} + \underset{base}{NaOH_{(s)}} \xrightarrow{H_2O} \underset{salt}{H_2OCH_3CO_2Na_{(aq)}} + \underset{water}{H_2O_{(l)}}$$

Depending on the acid–base properties of its component ions, however, a salt can dissolve in water to produce a neutral solution, a basic solution, or an acidic solution.

When a salt such as $NaCl$ dissolves in water, it produces $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ ions. Using a Lewis approach, the Na^+ ion can be viewed as an acid because it is an electron pair acceptor, although its low charge and relatively large radius make it a very weak acid. The Cl^- ion is the conjugate base of the strong acid HCl, so it has essentially no basic character. Consequently, dissolving $NaCl$ in water has no effect on the pH of a solution, and the solution remains neutral.

Now let's compare this behavior to the behavior of aqueous solutions of potassium cyanide and sodium acetate. Again, the cations (K^+ and Na^+) have essentially no acidic character, but the anions (CN^- and $CH_3CO_2^-$) are weak bases that can react with water because they are the conjugate bases of the weak acids HCN and acetic acid, respectively.

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$$

$$CH_3CO^2_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)}$$

Neither reaction proceeds very far to the right as written because the formation of the weaker acid–base pair is favored. Both HCN and acetic acid are stronger acids than water, and hydroxide is a stronger base than either acetate or cyanide, so in both cases, the equilibrium lies to the left. Nonetheless, each of these reactions generates enough hydroxide ions to produce a basic solution. For example, the pH of a 0.1 M solution of sodium acetate or potassium cyanide at 25°C is 8.8 or 11.1, respectively. From Table 16.9.1 and Figure 16.9.1, we can see that CN^- is a stronger base ($pK_b = 4.79$) than acetate ($pK_b = 9.24$), which is consistent with KCN producing a more basic solution than sodium acetate at the same concentration.

In contrast, the conjugate acid of a weak base should be a weak acid (Equation 16.9.1). For example, ammonium chloride and pyridinium chloride are salts produced by reacting ammonia and pyridine, respectively, with HCl. As you already know, the chloride ion is such a weak base that it does not react with water. In contrast, the cations of the two salts are weak acids that react with water as follows:

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons HH_{3(aq)} + H_3O^+_{(aq)} \tag{16.9.1}$$

$$C_5H_5NH^+_{(aq)} + H_2O_{(l)} \rightleftharpoons C_5H_5NH_{(aq)} + H_3O^+_{(aq)} \tag{16.9.2}$$

Equation 16.9.1 indicates that H_3O^+ is a stronger acid than either NH_4^+ or $C_5H_5NH^+$, and conversely, ammonia and pyridine are both stronger bases than water. The equilibrium will therefore lie far to the left in both cases, favoring the weaker acid–base pair. The H_3O^+ concentration produced by the reactions is great enough, however, to decrease the pH of the solution significantly: the pH of a 0.10 M solution of ammonium chloride or pyridinium chloride at 25°C is 5.13 or 3.12, respectively. This is consistent with the information shown in Figure 16.2, indicating that the pyridinium ion is more acidic than the ammonium ion.

What happens with aqueous solutions of a salt such as ammonium acetate, where both the cation and the anion can react separately with water to produce an acid and a base, respectively? According to Figure 16.10, the ammonium ion will lower the pH, while according to Equation 16.9.2, the acetate ion will raise the pH. This particular case is unusual, in that the cation is as strong an acid as the anion is a base (pKa ≈ pKb). Consequently, the two effects cancel, and the solution remains neutral. With

salts in which the cation is a stronger acid than the anion is a base, the final solution has a $pH < 7.00$. Conversely, if the cation is a weaker acid than the anion is a base, the final solution has a $pH > 7.00$.

Solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion (part (a) in Figure 16.9.1). A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.

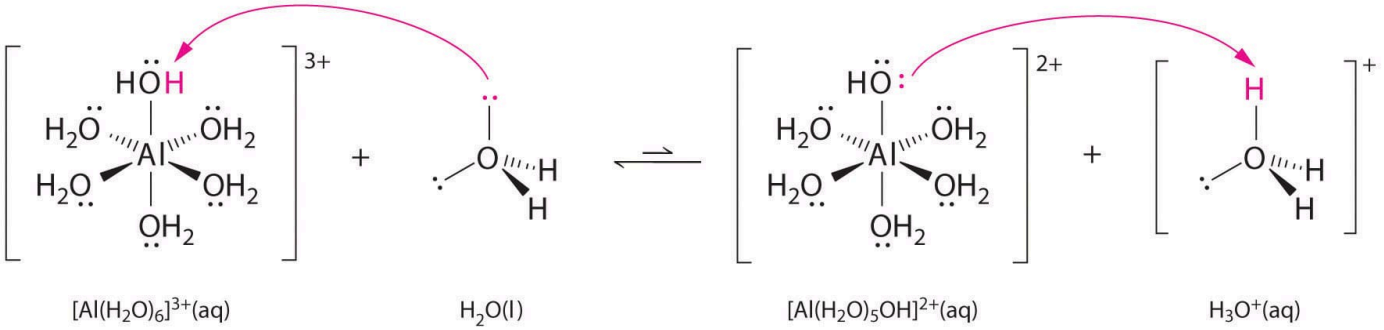


Figure 16.9.1. With less electron density between the O atoms and the H atoms, the $\mathrm{O{-}H}$ bonds are weaker than in a free H_2O molecule, making it easier to lose a H^+ ion.

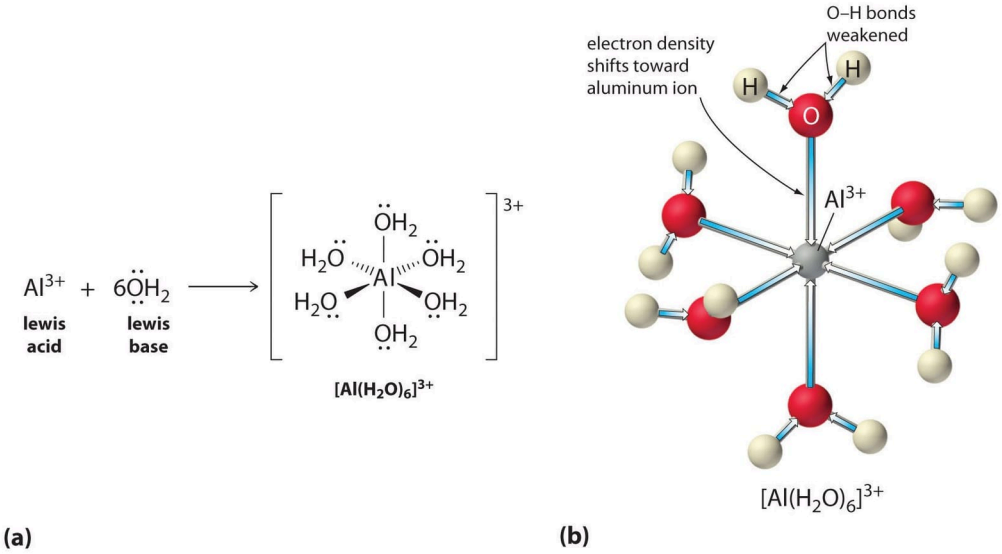


Figure 16.9.1: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton.

On the left is the reaction of Al three plus with six OH2 which produces [AL(H2O)6] three plus. On the right is the molecular structure of [Al(H2O)6] three plus.

The magnitude of this effect depends on the following two factors (Figure 16.9.2):

1. The charge on the metal ion. A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^+) of the same radius.
2. The radius of the metal ion. For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

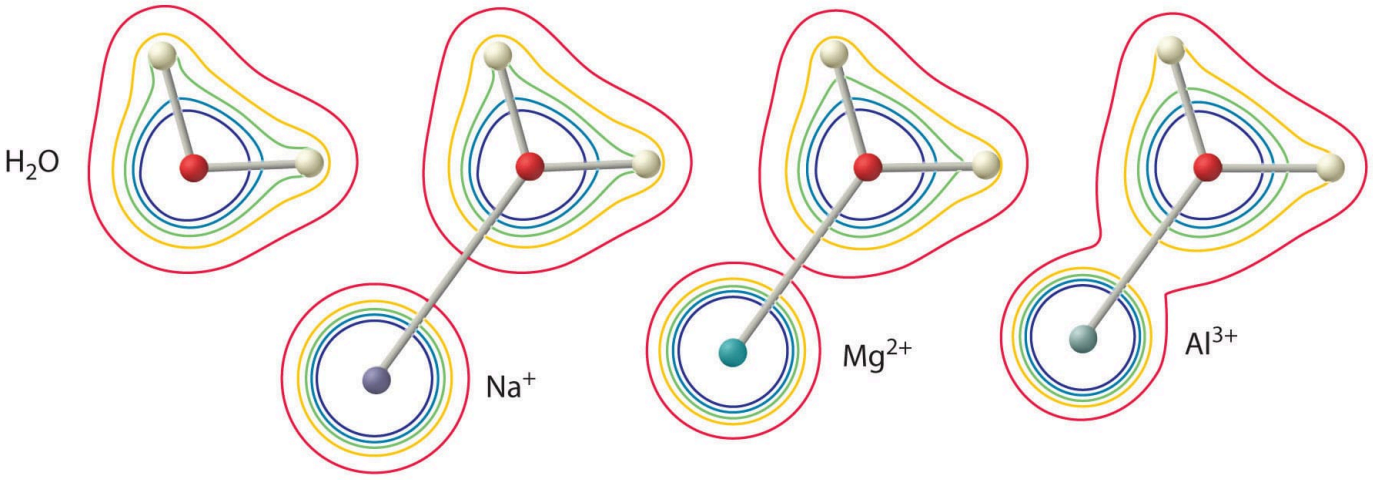


Figure 16.9.2: The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^+, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases.

Thus aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+}, are acidic:

$$[Al(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)} \tag{16.9.3}$$

The $[Al(H_2O)_6]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameter for predicting the effect of a metal ion on the acidity of coordinated water molecules is the charge-to-radius ratio of the metal ion. A number of pairs of metal ions that lie on a diagonal line in the periodic table, such as Li^+ and Mg^{2+} or Ca^{2+} and Y^{3+}, have different sizes and charges, but similar charge-to-radius ratios. As a result, these pairs of metal ions have similar effects on the acidity of coordinated water molecules, and they often exhibit other significant similarities in chemistry as well.

Solutions of small, highly charged metal ions in water are acidic.

Reactions such as those discussed in this section, in which a salt reacts with water to give an acidic or basic solution, are often called hydrolysis reactions. Using a separate name for this type of reaction is unfortunate because it suggests that they are somehow different. In fact, hydrolysis reactions are just acid–base reactions in which the acid is a cation or the base is an anion; they obey the same principles and rules as all other acid–base reactions.

A hydrolysis reaction is an acid–base reaction.

Example 16.9.1

Predict whether aqueous solutions of these compounds are acidic, basic, or neutral.

a. KNO_3
b. $CrBr_3 cdot H_2O$
c. Na_2SO_4

Given: compound

Asked for: acidity or basicity of aqueous solution

Strategy:

A. Assess the acid–base properties of the cation and the anion. If the cation is a weak Lewis acid, it will not affect the pH of the solution. If the cation is the conjugate acid of a weak base or a relatively highly charged metal cation, however, it will react with water to produce an acidic solution.
B. f the anion is the conjugate base of a strong acid, it will not affect the pH of the solution. If, however, the anion is the conjugate base of a weak acid, the solution will be basic.

Solution:

a

A. The K^+ cation has a small positive charge (+1) and a relatively large radius (because it is in the fourth row of the periodic table), so it is a very weak Lewis acid.
B. The $NO_3\ -$ anion is the conjugate base of a strong acid, so it has essentially no basic character (Table 16.1). Hence neither the cation nor the anion will react with water to produce H^+ or OH^-, and the solution will be neutral.

b.

A. The Cr^{3+} ion is a relatively highly charged metal cation that should behave similarly to the Al^{3+} ion and form the $[Cr(H2O)_6]^{3+}$ complex, which will behave as a weak acid:

$$Cr(H_2O)_{6]^{3+}_{(aq)}} \rightleftharpoons Cr(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)}$$

B. The Br^- anion is a very weak base (it is the conjugate base of the strong acid HBr), so it does not affect the pH of the solution. Hence the solution will be acidic.

c.

A. The Na^+ ion, like the K^+, is a very weak acid, so it should not affect the acidity of the solution.
B. In contrast, SO_4^{2-} is the conjugate base of HSO_4^-, which is a weak acid. Hence the SO_4^{2-} ion will react with water as shown in Figure 16.6 to give a slightly basic solution.

Exercise 16.9.1

Predict whether aqueous solutions of the following are acidic, basic, or neutral.

a. KI
b. $Mg(ClO_4)_2$
c. $NaHS$

Answer a available at the end of this section.

Summary

A salt can dissolve in water to produce a neutral, a basic, or an acidic solution, depending on whether it contains the conjugate base of a weak acid as the anion (A^-), the conjugate acid of a weak base as the cation (BH^+), or both. Salts that contain small, highly charged metal ions produce acidic solutions in water. The reaction of a salt with water to produce an acidic or a basic solution is called a hydrolysis reaction.

Key Takeaways

- Acid–base reactions always contain two conjugate acid–base pairs.
- Each acid and each base has an associated ionization constant that corresponds to its acid or base strength.

Answers

Exercise 16.9.1

neutral
acidic
basic (due to the reaction of $\mathrm{HS^-}$ with water to form $\mathrm{H_2S}$ and $\mathrm{OH^-}$)

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16.10: Acid-Base Behavior and Chemical Structure

Learning Objectives

- To understand how molecular structure affects the strength of an acid or base.

We have seen that the strengths of acids and bases vary over many orders of magnitude. In this section, we explore some of the structural and electronic factors that control the acidity or basicity of a molecule.

Bond Strengths

In general, the stronger the $\mathrm{A{-}H}$ or $\mathrm{B{-}H^+}$ bond, the less likely the bond is to break to form H^+ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
H–X Bond Energy (kJ/mol)	570	432	366	298
pKa	3.20	−6.1	−8.9	−9.3

The trend in bond energies is due to a steady decrease in overlap between the 1s orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, acid strengths of binary hydrides increase as we go down a column of the periodic table. For example, the order of acidity for the binary hydrides of Group 16 elements is as follows, with pK_a values in parentheses:

$$H_2O(14.00 = pK_w) < H_2S(7.05) < H_2Se(3.89) < H_2Te(2.6) \tag{16.10.1}$$

Stability of the Conjugate Base

Whether we write an acid–base reaction as $AH \rightleftharpoons A^- + H^+$ or as $BH^+ \rightleftharpoons B + H^+$, the conjugate base ($A^-$ or B) contains one more lone pair of electrons than the parent acid (AH or BH^+). Any factor that stabilizes the lone pair on the conjugate base favors dissociation of H^+ and makes the parent acid a stronger acid. Let's see how this explains the relative acidity of the binary hydrides of the elements in the second row of the periodic table. The observed order of increasing acidity is the following, with pKa values in parentheses:

$$CH_4(\ 50) \ll NH_3(\ 36) < H_2O(14.00) < HF(3.20) \tag{16.10.2}$$

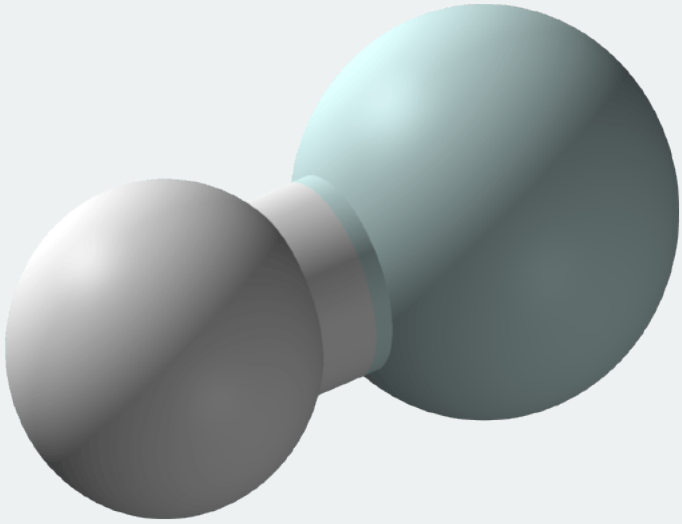
Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH_4 is CH_3^-, and the conjugate base of HF is F^-. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the F^- ion than carbon can stabilize the negative charge in the CH3– ion. Consequently, HF has a greater tendency to dissociate to form H^+ and F^- than does methane to form H^+ and CH_3^-, making HF a much stronger acid than CH_4.

The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form E^- and H^+. Due to both the increasing stability of the conjugate base and the increasing polarization of the E–H bond in the conjugate acid, acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table.

> Acid strengths of binary hydrides increase as we go down a column or from left to right across a row of the periodic table.

the strongest acid Known: The hydrohelium Cation

The storngер acid, the weaker the covalent bond to a hydrogen atom. So the strongest acid possible is the molecule with the weakest bond. That is the hydrohelium (1+) cation, $\mathrm{HeH^+}$, which is a positively charged ion formed by the reaction of a proton with a helium atom in the gas phase. It was first produced in the laboratory in 1925 and is isoelectronic with molecular hydrogen (\ce{H2}). It is the strongest known acid, with a proton affinity of 177.8 kJ/mol.



Ball and stick model of the hydrohelium ion. (CC BY-SA 3.0; CCoil).

$\mathrm{HeH^+}$ cannot be prepared in a condensed phase, as it would protonate any anion, molecule or atom with which it were associated. However it is possible to estimate a *hypothetical* aqueous acidity using Hess's law:

$HHe^+(g)$	→	$H^+(g)$	+ He(*g*)	+178 kJ/mol
$HHe^+(aq)$	→	$HHe^+(g)$		+973 kJ/mol
$H^+(g)$	→	$H^+(aq)$		–1530 kJ/mol
He(*g*)	→	He(*aq*)		+19 kJ/mol
$HHe^+(aq)$	→	$H^+(aq)$	+ He(*aq*)	–360 kJ/mol

A free energy change of dissociation of –360 kJ/mol is equivalent to a pK_a of –63.

It has been suggested that $\mathrm{HeH^+}$ should occur naturally in the interstellar medium, but it has not yet been detected.

Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of electrons within the molecule. This is called an inductive effect, and, much like the coordination of water to a metal ion, it can have a major effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:

$$HOX_{(aq)} \rightleftharpoons H^+_{(aq)} + OX^-(aq) \tag{16.10.3}$$

The acidities of these acids vary by about three orders of magnitude, however, due to the difference in electronegativity of the

halogen atoms:

HOX	Electronegativity of X	pKa
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

As the electronegativity of X increases, the distribution of electron density within the molecule changes: the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond and allowing dissociation of hydrogen as H^+.

The acidity of oxoacids, with the general formula $HOXO_n$ (with n = 0–3), depends strongly on the number of terminal oxygen atoms attached to the central atom X. As shown in Figure $16.10.1$, the K_a values of the oxoacids of chlorine increase by a factor of about 10^4 to 10^6 with each oxygen as successive oxygen atoms are added. The increase in acid strength with increasing number of terminal oxygen atoms is due to both an inductive effect and increased stabilization of the conjugate base.

Any inductive effect that withdraws electron density from an O–H bond increases the acidity of the compound.

Because oxygen is the second most electronegative element, adding terminal oxygen atoms causes electrons to be drawn away from the O–H bond, making it weaker and thereby increasing the strength of the acid. The colors in Figure $16.10.1$ show how the electrostatic potential, a measure of the strength of the interaction of a point charge at any place on the surface of the molecule, changes as the number of terminal oxygen atoms increases. In Figure $16.10.1$ and Figure $16.10.2$, blue corresponds to low electron densities, while red corresponds to high electron densities. The oxygen atom in the O–H unit becomes steadily less red from $HClO$ to $HClO_4$ (also written as $HOClO_3$, while the H atom becomes steadily bluer, indicating that the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. The decrease in electron density in the O–H bond weakens it, making it easier to lose hydrogen as H^+ ions, thereby increasing the strength of the acid.

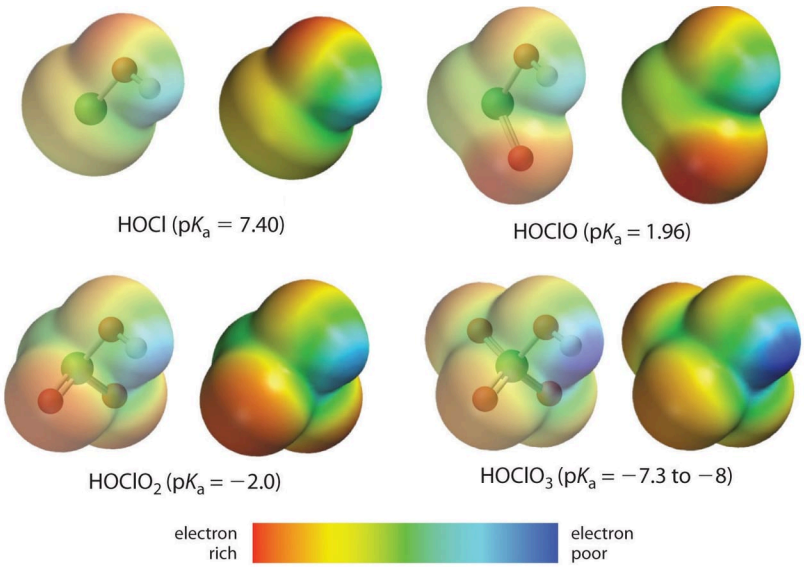
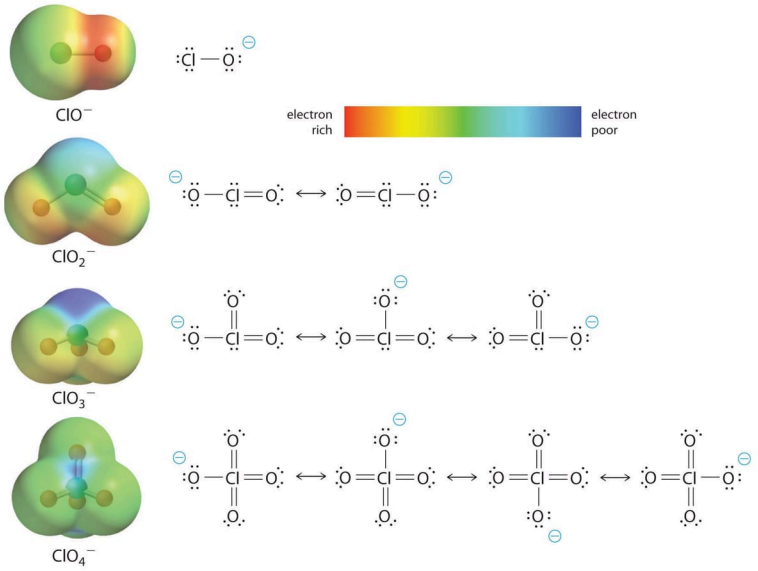


Figure $16.10.1$: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit. These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities. Source: Chlorine oxoacids pKa values from J. R. Bowser, Inorganic Chemistry (Pacific Grove, CA: Brooks-Cole,1993).

At least as important, however, is the effect of delocalization of the negative charge in the conjugate base. As shown in Figure $16.10.2$, the number of resonance structures that can be written for the oxoanions of chlorine increases as the number of terminal oxygen atoms increases, allowing the single negative charge to be delocalized over successively more oxygen atoms.

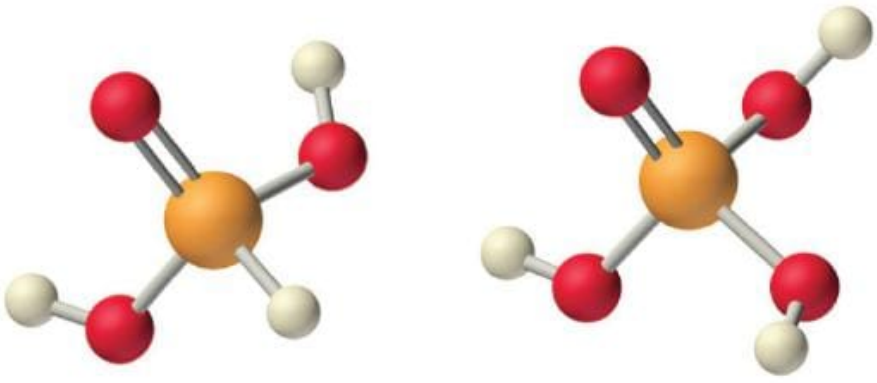
Electron delocalization in the conjugate base increases acid strength.

The electrostatic potential plots in Figure $16.10.2$ demonstrate that the electron density on the terminal oxygen atoms decreases steadily as their number increases. The oxygen atom in ClO– is red, indicating that it is electron rich, and the color of oxygen progressively changes to green in ClO_4^+, indicating that the oxygen atoms are becoming steadily less electron rich through the series. For example, in the perchlorate ion (ClO_4^-), the single negative charge is delocalized over all four oxygen atoms, whereas in the hypochlorite ion (OCl^-), the negative charge is largely localized on a single oxygen atom (Figure $16.10.2$). As a result, the perchlorate ion has no localized negative charge to which a proton can bind. Consequently, the perchlorate anion has a much lower affinity for a proton than does the hypochlorite ion, and perchloric acid is one of the strongest acids known.



As the number of terminal oxygen atoms increases, the number of resonance structures that can be written for the oxoanions of chlorine also increases, and the single negative charge is delocalized over more oxygen atoms. As these electrostatic potential plots demonstrate, the electron density on the terminal oxygen atoms decreases steadily as their number increases. As the electron density on the oxygen atoms decreases, so does their affinity for a proton, making the anion less basic. As a result, the parent oxoacid is more acidic.

Similar inductive effects are also responsible for the trend in the acidities of oxoacids that have the same number of oxygen atoms as we go across a row of the periodic table from left to right. For example, H_3PO_4 is a weak acid, H_2SO_4 is a strong acid, and $HClO_4$ is one of the strongest acids known. The number of terminal oxygen atoms increases steadily across the row, consistent with the observed increase in acidity. In addition, the electronegativity of the central atom increases steadily from P to S to Cl, which causes electrons to be drawn from oxygen to the central atom, weakening the $\mathrm{O{-}H}$ bond and increasing the strength of the oxoacid.



Careful inspection of the data in Table 16.10.1 shows two apparent anomalies: carbonic acid and phosphorous acid. If carbonic acid (H_2CO_3) were a discrete molecule with the structure $(HO)_2C{=}O$, it would have a single terminal oxygen atom and should be comparable in acid strength to phosphoric acid (H_3PO_4), for which pKa1 = 2.16. Instead, the tabulated value of pK_{a1} for carbonic acid is 6.35, making it about 10,000 times weaker than expected. As we shall see, however, H_2CO_3 is only a minor component of the aqueous solutions of CO_2 that are referred to as carbonic acid. Similarly, if phosphorous acid (H_3PO_3) actually had the structure $(HO)_3P$, it would have no terminal oxygen atoms attached to phosphorous. It would therefore be expected to be about as strong an acid as $HOCl$ (pKa = 7.40). In fact, the pK_{a1} for phosphorous acid is 1.30, and the structure of phosphorous acid is $(HO)_2P(=O)H$ with one H atom directly bonded to P and one $P{=}O$ bond. Thus the pKa1 for phosphorous acid is similar to that of other oxoacids with one terminal oxygen atom, such as H_3PO_4. Fortunately, phosphorous acid is the only common oxoacid in which a hydrogen atom is bonded to the central atom rather than oxygen.

Table 16.10.1: Values of pKa for Selected Polyprotic Acids and Bases

Polyprotic Acids	Formula	pK_{a1}	pK_{a2}	pK_{a3}
carbonic acid*	"H_2CO_3"	6.35	10.33	
citric acid	$HO_2CCH-2C(OH)(CO_2H)CH_2CO_2H$	3.13	4.76	6.40
malonic acid	$HO-2CCH_2CO_2H$	2.85	5.70	
oxalic acid	HO_2CCO_2H	1.25	3.81	
phosphoric acid	H_3PO_4	2.16	7.21	12.32
phosphorous acid	H_3PO_3	1.3	6.70	
succinic acid	$HO_2CCH_2CH_2CO_2H$	4.21	5.64	
sulfuric acid	H_2SO_4	–2.0	1.99	
sulfurous acid*	"H_2SO_3"	1.85	7.21	
Polyprotic Bases	**Formula**	pK_{b1}	pK_{b2}	
ethylenediamine	$H_2N(CH_2)_2NH_2$	4.08	7.14	
piperazine	$HN(CH_2CH_2)_2NH$	4.27	8.67	
propylenediamine	$H_2N(CH_2)_3NH_2$	3.45	5.12	

***H_2CO_3 and H_2SO_3 are at best minor components of aqueous solutions of $CO_{2(g)}$ and $SO_{2(g)}$, respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.**

Inductive effects are also observed in organic molecules that contain electronegative substituents. The magnitude of the

electron-withdrawing effect depends on both the nature and the number of halogen substituents, as shown by the pKa values for several acetic acid derivatives:

\[pK_a CH_3CO_2H 4.76< CH_2ClCO_2H 2.87

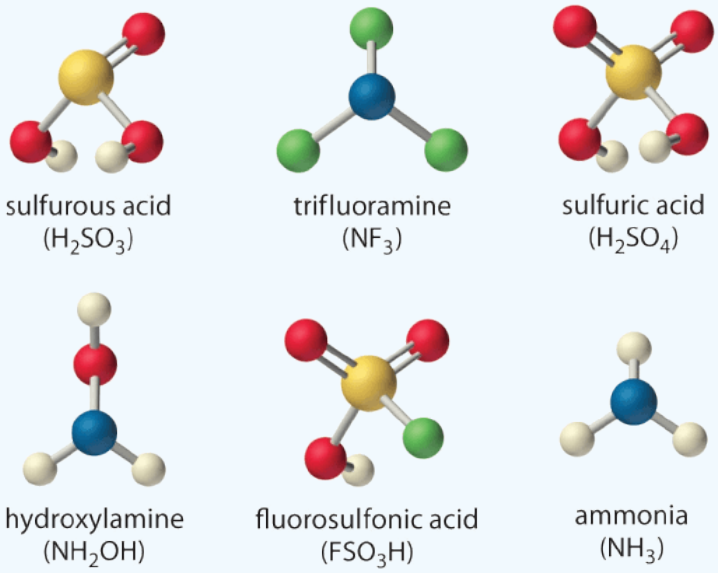
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $-\mathrm{CH_3}$ group of acetic acid by a $-\mathrm{CF_3}$ group results in about a 10,000-fold increase in acidity!

Example 16.10.1

Arrange the compounds of each series in order of increasing acid or base strength.

a. sulfuric acid [H_2SO_4, or $(HO)_2SO_2$], fluorosulfonic acid (FSO_3H, or FSO_2OH), and sulfurous acid [H_2SO_3, or $(HO)_2SO$]
b. ammonia (NH_3), trifluoramine (NF_3), and hydroxylamine (NH_2OH)

The structures are shown here.



Given: series of compounds

Asked for: relative acid or base strengths

Strategy:

Use relative bond strengths, the stability of the conjugate base, and inductive effects to arrange the compounds in order of increasing tendency to ionize in aqueous solution.

Solution:

Although both sulfuric acid and sulfurous acid have two –OH groups, the sulfur atom in sulfuric acid is bonded to two terminal oxygen atoms versus one in sulfurous acid. Because oxygen is highly electronegative, sulfuric acid is the stronger acid because the negative charge on the anion is stabilized by the additional oxygen atom. In comparing sulfuric acid and fluorosulfonic acid, we note that fluorine is more electronegative than oxygen. Thus replacing an –OH by –F will remove more electron density from the central S atom, which will, in turn, remove electron density from the S–OH bond and the O–H bond. Because its O–H bond is weaker, FSO_3H is a stronger acid than sulfuric acid. The predicted order of acid strengths given here is confirmed by the measured pKa values for these acids:

\[pKa H_2SO_3 1.85

The structures of both trifluoramine and hydroxylamine are similar to that of ammonia. In trifluoramine, all of the hydrogen atoms in NH3 are replaced by fluorine atoms, whereas in hydroxylamine, one hydrogen atom is replaced by OH. Replacing the three hydrogen atoms by fluorine will withdraw electron density from N, making the lone electron pair on N less available to bond to an H^+ ion. Thus NF_3 is predicted to be a much weaker base than NH_3. Similarly, because oxygen is more electronegative than hydrogen, replacing one hydrogen atom in NH_3 by OH will make the amine less basic. Because oxygen is less electronegative than fluorine and only one hydrogen atom is replaced, however, the effect will be smaller. The predicted order of increasing base strength shown here is confirmed by the measured pK_b values:

\[pK_bNF_3—<

Trifluoramine is such a weak base that it does not react with aqueous solutions of strong acids. Hence its base ionization constant has never been measured.

Exercise 16.10.1

Arrange the compounds of each series in order of

a. decreasing acid strength: H_3PO_4, $CH_3PO_3H_2$, and $HClO_3$.
b. increasing base strength: CH_3S^-, OH^-, and CF_3S^-.

Answer a available at the end of this section.

Summary

Inductive effects and charge delocalization significantly influence the acidity or basicity of a compound. The acid–base strength of a molecule depends strongly on its structure. The weaker the A–H or B–H+ bond, the more likely it is to dissociate to form an H^+ ion. In addition, any factor that stabilizes the lone pair on the conjugate base favors the dissociation of H^+, making the conjugate acid a stronger acid. Atoms or groups of atoms elsewhere in a molecule can also be important in determining acid or base strength through an inductive effect, which can weaken an $\mathrm{O—H}$ bond and allow hydrogen to be more easily lost as H^+ ions.

Contributors and Attributions

- ◦ Anonymous

Answers

Exercise 16.10.1

$HClO-3 > CH_3PO_3H_2 > H_3PO_4$

$CF_3S^- < CH_3S^- < OH^-$

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16.11: Lewis Acids and Bases

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- Write the equation for the proton transfer reaction involving a Brønsted-Lowry acid or base, and show how it can be interpreted as an electron-pair transfer reaction, clearly identifying the donor and acceptor.
- Give an example of a *Lewis acid-base reaction* that does not involve protons.
- Write equations illustrating the behavior of a given non-aqueous acid-base system.

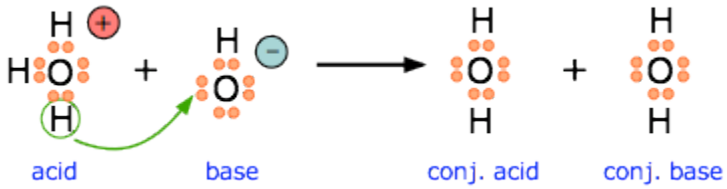
The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. According to Lewis,

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.

Proton-Transfer Reactions Involve Electron-Pair Transfer

Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.

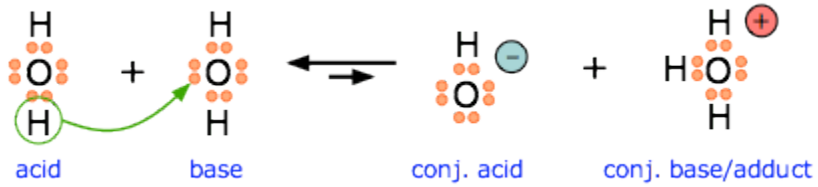


This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

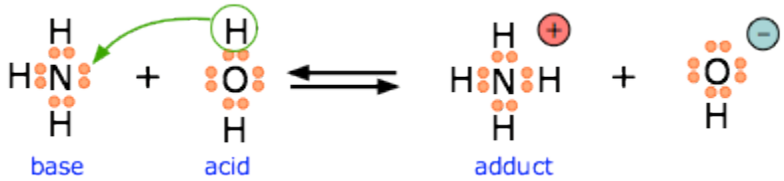
- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note carefully that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product of a Lewis acid-base reaction is known formally as an "adduct" or

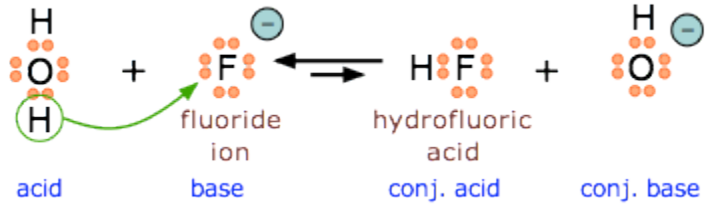
"complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.



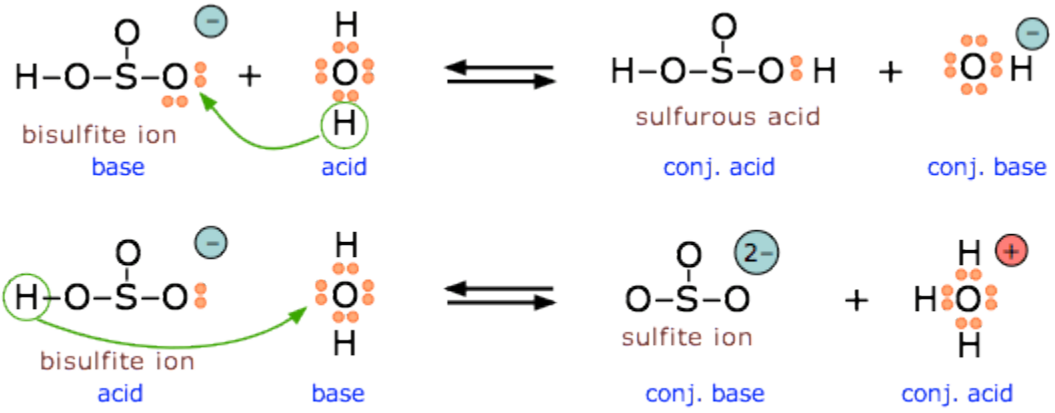
Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.



Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^- accepts a proton from water, which is transformed into a hydroxide ion.



The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.

Acid-base Reactions without Transferring Protons

The major utility of the Lewis definition is that it extends the concept of acids and bases beyond the realm of proton transfer reactions. The classic example is the reaction of boron trifluoride with ammonia to form an *adduct*:

$$BF_3 + NH_3 \rightarrow F_3B{-}NH_3 \tag{16.11.1}$$

One of the most commonly-encountered kinds of Lewis acid-base reactions occurs when electron-donating ligands form coordination complexes with transition-metal ions.

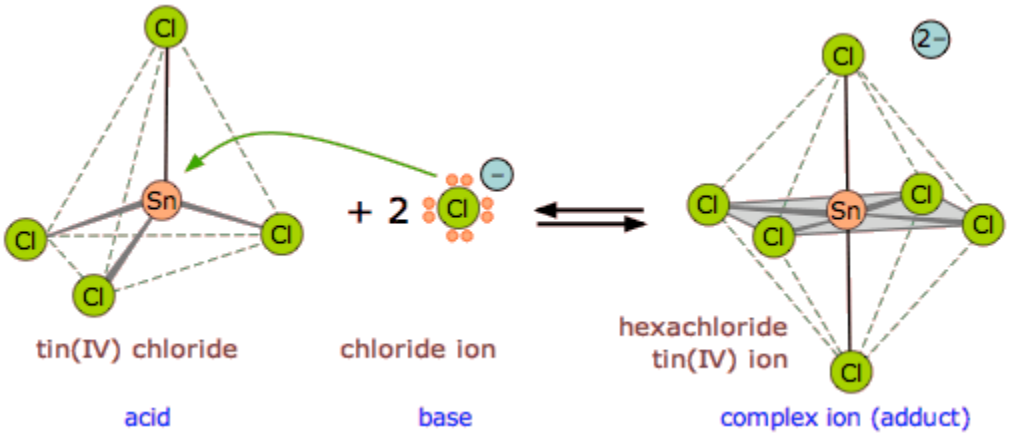


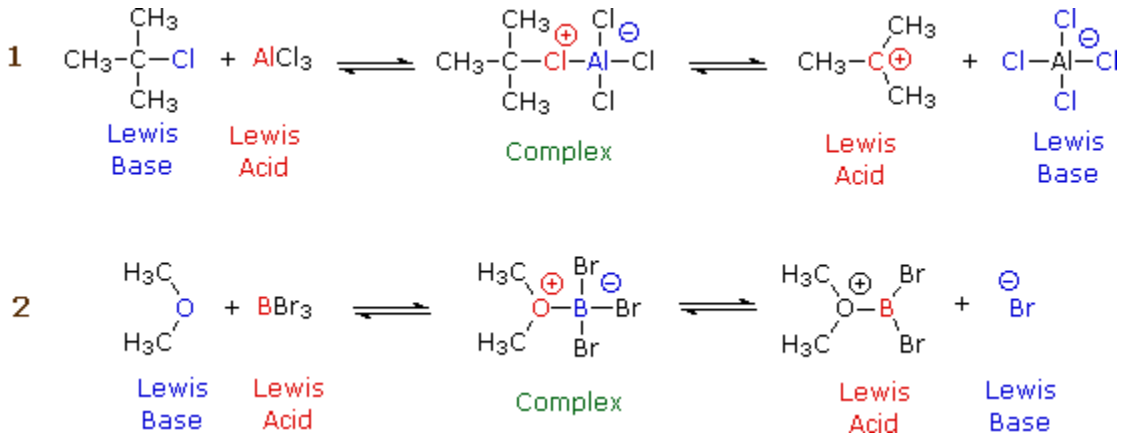
Figure 16.11.1: The tin atom in $SnCl_4$ can expand its valence shell by utilizing a pair of d-orbitals, changing its hybridization from sp^3 to sp^3d^2.

Exercise 16.11.1

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4{}^-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3{}^{2-}$
c. $Cd(CN)_2 + 2\,CN^- \rightarrow Cd(CN)_4{}^{2+}$
d. $AgCl + 2\,NH_3 \rightarrow Ag(NH_3)_2{}^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $Ni^{2+} + 6\,NH_3 \rightarrow Ni(NH_3)_5{}^{2+}$

Although organic chemistry is beyond the scope of these lessons, it is instructive to see how electron donors and acceptors play a role in chemical reactions. The following two diagrams show the mechanisms of two common types of reactions initiated by simple inorganic Lewis acids:



In each case, the species labeled "Complex" is an intermediate that decomposes into the products, which are conjugates of the original acid and base pairs. The electric charges indicated in the complexes are formal charges, but those in the products are

"real".

In reaction 1, the incomplete octet of the aluminum atom in $AlCl_3$ serves as a better electron acceptor to the chlorine atom than does the isobutyl part of the base. In reaction 2, the pair of non-bonding electrons on the dimethyl ether coordinates with the electron-deficient boron atom, leading to a complex that breaks down by releasing a bromide ion.

Non-aqueous Protonic Acid-Base Systems

We ordinarily think of Brønsted-Lowry acid-base reactions as taking place in aqueous solutions, but this need not always be the case. A more general view encompasses a variety of acid-base *solvent systems*, of which the *water system* is only one (Table 16.11.1). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The ammonia system is one of the most common non-aqueous system in Chemistry. Liquid ammonia boils at –33° C, and can conveniently be maintained as a liquid by cooling with dry ice (–77° C). It is a good solvent for substances that also dissolve in water, such as ionic salts and organic compounds since it is capable of forming hydrogen bonds. However, many other familiar substances can also serve as the basis of protonic solvent systems as Table 16.11.1 indicates:

Table 16.11.1: Popular Solvent systems

solvent	autoprotolysis reaction	pK_{ap}
water	$2\ H_2O \rightarrow H_3O^+ + OH^-$	14
ammonia	$2\ NH_3 \rightarrow NH_4^+ + NH_2^-$	33
acetic acid	$2\ CH_3COOH \rightarrow CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2\ C_2H_5OH \rightarrow C_2H_5OH_2^+ + C_2H_5O^-$	19
hydrogen peroxide	$2\ HO\text{-}OH \rightarrow HO\text{-}OH_2^+ + HO\text{-}O^-$	13
hydrofluoric acid	$2\ HF \rightarrow H_2F^+ + F^-$	10
sulfuric acid	$2\ H_2SO_4 \rightarrow H_3SO_4^+ + HSO_4^-$	3.5

One use of nonaqueous acid-base systems is to examine the relative strengths of the strong acids and bases, whose strengths are "leveled" by the fact that they are all totally converted into H_3O^+ or OH^- ions in water. By studying them in appropriate non-aqueous solvents which are poorer acceptors or donors of protons, their relative strengths can be determined.

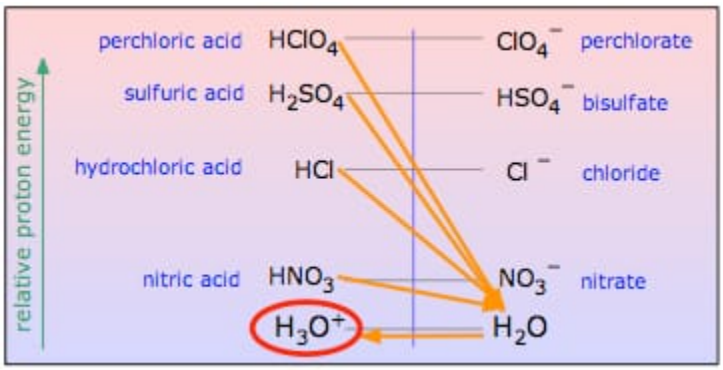


Figure 16.11.2: Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling" of the solvent.

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16.E: Acid–Base Equilibria (Exercises)

16.1: Acids and Bases: A Brief Review

16.2: Brønsted–Lowry Acids and Bases

Conceptual Problems

1. Identify the conjugate acid–base pairs in each equilibrium.
   a. $HSO_4^-\ (aq) + H_2O\ (l) \rightleftharpoons SO_4^{2-}\ (aq) + H_3O^+\ (aq)$
   b. $C_3H_7NO_2\ (aq) + H_3O^+\ (aq) \rightleftharpoons C_3H_8NO_2^+\ (aq) + H_2O\ (l)$
   c. $CH_3O_2H\ (aq) + NH_3\ (aq) \rightleftharpoons CH_3CO_2^-\ (aq) + NH_4^+\ (aq)$
   d. $SbF_5\ (aq) + 2\ HF\ (aq) \rightleftharpoons H_2F^+\ (aq) + SbF_6^-\ (aq)$
2. Identify the conjugate acid–base pairs in each equilibrium.
   a. $HF\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + F^-\ (aq)$
   b. $CH_3CH_2NH_2\ (aq) + H_2O\ (l) \rightleftharpoons CH_3CH_2NH_3^+\ (aq) + OH^-\ (aq)$
   c. $C_3H_7NO_2\ (aq) + OH^-\ (aq) \rightleftharpoons C_3H_6NO_2^-\ (aq) + H_2O\ (l)$
   d. $CH_3CO_2H\ (aq) + 2\ HF\ (aq) \rightleftharpoons CH_3C(OH)_2^+\ (aq) + HF_2^-\ (aq)$
3. Salts such as NaH contain the hydride ion (H^-). When sodium hydride is added to water, it produces hydrogen gas in a highly vigorous reaction. Write a balanced chemical equation for this reaction and identify the conjugate acid–base pairs.
4. Write the expression for K_a for each reaction.
   a. $HCO_3^-\ (aq) + H_2O\ (l) \rightleftharpoons CO_3^{2-}\ (aq) + H_3O^+\ (aq)$
   b. $formic\ acid\ (aq) + H_2O\ (l) \rightleftharpoons formate\ (aq) + H_3O^+\ (aq)$
   c. $H_3PO_4\ (aq) + H_2O\ (l) \rightleftharpoons H_2PO_4^-\ (aq) + H_3O^+\ (aq)$
5. Write an expression for the ionization constant K_b for each reaction.
   a. $OCH_3^-\ (aq) + H_2O\ (l) \rightleftharpoons HOCH_3\ (aq) + OH^-\ (aq)$
   b. $NH_2^-\ (aq) + H_2O\ (l) \rightleftharpoons NH_3\ (aq) + OH^-\ (aq)$
   c. $S^{2-}\ (aq) + H_2O\ (l) \rightleftharpoons HS^-\ (aq) + OH^-\ (aq)$
6. Predict whether each equilibrium lies primarily to the left or to the right.
   a. $HBr\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + Br^-\ (aq)$
   b. $NaH\ (s) + NH_3\ (aq) \rightleftharpoons H_2\ (g) + NaNH_2\ (s)$
   c. $OCH_3^-\ (aq) + NH_3\ (aq) \rightleftharpoons CH_3OH\ (aq) + NH_2^-\ (aq)$
   d. $NH_3\ (aq) + HCl\ (aq) \rightleftharpoons NH_4^+\ (aq) + Cl^-\ (aq)$
7. Species that are strong bases in water, such as CH_3^-, NH_2^-, and S^{2-}, are leveled to the strength of OH^-, the conjugate base of H_2O. Because their relative base strengths are indistinguishable in water, suggest a method for identifying which is the strongest base. How would you distinguish between the strength of the acids HIO_3, H_2SO_4, and $HClO_4$?
8. Is it accurate to say that a 2.0 M solution of H_2SO_4, which contains two acidic protons per molecule, is 4.0 M in H^+? Explain your answer.
9. The alkalinity of soil is defined by the following equation: alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$. The source of both HCO_3^- and CO_3^{2-} is H_2CO_3. Explain why the basicity of soil is defined in this way.
10. Why are aqueous solutions of salts such as $CaCl_2$ neutral? Why is an aqueous solution of $NaNH_2$ basic?
11. Predict whether the aqueous solutions of the following are acidic, basic, or neutral.
    a. Li_3N
    b. NaH
    c. KBr
    d. $C_2H_5NH_3Cl$
12. When each compound is added to water, would you expect the pH of the solution to increase, decrease, or remain the same?
    a. $LiCH_3$
    b. $MgCl_2$
    c. K_2O
    d. $(CH_3)_2NH_2^+Br^-$
13. Which complex ion would you expect to be more acidic: $Pb(H_2O)_4^{2+}$ or $Sn(H_2O)_4^{2+}$? Why?
14. Would you expect $Sn(H_2O)_4^{2+}$ or $Sn(H_2O)_6^{4+}$ to be more acidic in aqueous solutions? Why?

15. Is it possible to arrange the hydrides LiH, RbH, KH, CsH, and NaH in order of increasing base strength in aqueous solution? Why or why not?

Conceptual Answer

1.

a. $\underset{\text{acid}}{HSO_4^-}(aq) + \underset{\text{base}}{H_2O}(l) \rightleftharpoons \underset{\text{conjugate base}}{SO_4^{2-}}(aq) + \underset{\text{conjugate acid}}{H_3O^+}(aq)$

b. $\underset{\text{base}}{C_3H_7NO_2}(aq) + \underset{\text{acid}}{H_3O^+}(aq) \rightleftharpoons \underset{\text{conjugate acid}}{C_3H_8NO_2^+}(aq) + \underset{\text{conjugate base}}{H_2O}(l)$

c. $\underset{\text{acid}}{HOAc}(aq) + \underset{\text{base}}{NH_3}(aq) \rightleftharpoons \underset{\text{conjugate base}}{CH_3CO_2^-}(aq) + \underset{\text{conjugate acid}}{NH_4^+}(aq)$

d. $\underset{\text{acid}}{SbF_5}(aq) + 2\,\underset{\text{base}}{HF}(aq) \rightleftharpoons \underset{\text{conjugate acid}}{H_2F^+}(aq) + \underset{\text{conjugate base}}{SbF_6^-}(aq)$

2.

a. $\underset{\text{acid}}{HF}(aq) + \underset{\text{base}}{H_2O}(l) \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+}(aq) + \underset{\text{conjugate base}}{F^-}(aq)$

b. $\underset{\text{base}}{CH_3CH_2NH_2}(aq) + \underset{\text{acid}}{H_2O}(l) \rightleftharpoons \underset{\text{conjugate acid}}{CH_3CH_2NH_3^+}(aq) + \underset{\text{conjugate base}}{OH^-}(aq)$

c. $\underset{\text{acid}}{C_3H_7NO_2}(aq) + \underset{\text{base}}{OH^-}(aq) \rightleftharpoons \underset{\text{conjugate base}}{C_3H_6NO_2^-}(aq) + \underset{\text{conjugate acid}}{H_2O}(l)$

d. $\underset{\text{base}}{CH_3CO_2H}(aq) + 2\,\underset{\text{acid}}{HF}(aq) \rightleftharpoons \underset{\text{conjugate acid}}{CH_3C(OH)_2^+}(aq) + \underset{\text{conjugate base}}{HF_2^-}(aq)$

3. $\underset{\text{base}}{NaH}(s) + \underset{\text{acid}}{H_2O}(l) \rightleftharpoons \underset{\text{conjugate acid}}{H_2}(g) + \underset{\text{conjugate base}}{NaOH}(aq)$

4.

a. $K_a = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$

b. $K_a = \frac{[formate][H_3O^+]}{[formic\ acid]}$

c. $K_a = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]}$

5.

a. $K_b = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$

b. $K_b = \frac{[NH_3][OH^-]}{[NH_2^-]}$

c. $K_b = \frac{[HS^-][OH^-]}{[S^{2-}]}$

6. Strong acids have the smaller pK_a.

a. Equilibrium lies primarily to the right because HBr ($pK_a = -8.7$) is a stronger acid than H_3O^+ ($pK_a = -1.7$) and H_2O ($pK_a = 14$) is a stronger base than Br^- ($pK_a = -8.7$).

b. Equilibrium lies primarily to the left because H_2 ($pK_a = 36$) is a stronger acid than NH_3 ($pK_a = 38$) and ($NaNH_2$) ($pK_a = 38$) is a stronger base than NaH ($pK_a = 35$).

c. Equilibrium lies primarily to the left because CH_3OH ($pK_a = 17$) is a stronger acid than NH_3 ($pK_a = 38$) and NH_2^- ($pK_a = 38$)

is a stronger base than OCH_3^- ($pK_a = 25$).

d. Equilibrium lies to the right because HCl ($pK_a = -7$) is a stronger acid than NH_4^+ ($pK_a = 9.3$) and NH_3 is a stronger base than Cl^- ($pK_a = -7$).

7. To identify the strongest base we can determine their weakest conjugate acid. The conjugate acids of CH_3^-, NH_2^-, and S_2^- are CH_4, NH_3, and HS^-, respectively. Next, we consider that acidity increases with positive charge on the molecule, thus ruling out that S_2^- is the weakest base. Finally, we consider that acidity increases with electronegativity, therefore NH_3 is the second most basic and CH_4 is the most basic. To distinguish between the strength of the acids HIO_3, H_2SO_4, and $HClO_4$ we can consider that the higher electronegativity and oxidation state of the central nonmetal is the more acidic, therefore the order of acidity is: HIO_3 <H_2SO_4<$HClO_4$ because electronegativity and oxidation state increases as follows: \(I(+5)

8. It is not accurate to say that a 2.0 M solution of H_2SO_4, which contains two acidic protons per molecule, is 4.0 M in H^+ because a 2.0 M solution of H_2SO_4 is equivalent to 4.0 N in H^+.

$$\frac{2.0\ mol\ H_2SO_4}{1\ L} \times \frac{2\ eq\ H^+}{1\ mol\ H_2SO_4} = \frac{4\ eq\ H^+}{L} = 4\ N\ H^+$$

9. Alkalinity is a measure of acid neutralizing capability. The basicity of the soil is defined this way because bases such as HCO_3^- and CO_3^{2-} can neutralize acids in soil. Because most soil has a pH between 6 and 8, alkalinity can be estimated by its carbonate species alone. At a near neutral pH, most carbonate species are bicarbonate.

10. Aqueous solutions of salts such as $CaCl_2$ are neutral because it is created from hydrochloric acid (a strong acid) and calcium hydroxide (a strong base). An aqueous solution of $NaNH_2$ is basic because it can deprotonate alkynes, alcohols, and a host of other functional groups with acidic protons such as esters and ketones.

11.

a. Li_3N is a base because the lone pair on the nitrogen can accept a proton.

b. NaH is a base because the hydrogen has a negative charge.

c. KBr is neutral because it is formed from HBr (a strong acid) and KOH (a strong base).

d. $C_2H_5NH_3Cl$ is acidic because it can donate a proton.

12.

a. The pH is expected to increase. $\underset{\text{acid}}{LiCH_3\,(aq)} + \underset{\text{base}}{H_2O\,(l)} \rightleftharpoons \underset{\text{conjugate base}}{LiOH\,(aq)} + \underset{\text{conjugate acid}}{CH_4\,(aq)}$

b. The pH is expected to increase. $\underset{\text{acid}}{MgCl_2\,(aq)} + \underset{\text{base}}{H_2O\,(l)} \rightleftharpoons \underset{\text{conjugate acid}}{2\,HCl\,(aq)} + \underset{\text{conjugate base}}{MgO\,(aq)}$

c. The pH is expected to remain the same. $K_2O\ (aq) + H_2O\ (l) \rightleftharpoons 2\ KOH\ (aq)$

d. The pH is expected to increase. $\underset{\text{acid}}{(CH_3)_2NH_2^+Br^-\,(aq)} + \underset{\text{base}}{H_2O\,(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+\,(aq)} + \underset{\text{conjugate base}}{(CH_3)_2NH\,(aq)}$

13. $Sn(H_2O)_4^{2+}$ is expected to be more acidic than $Pb(H_2O)_4^{2+}$ because Sn is more electronegative than Pb.

14. $Sn(H_2O)_6^{4+}$ is expected to be more acidic than $Sn(H_2O)_4^{2+}$ because the charge on Sn is greater ($4^+ > 2^+$).

15. Yes, it is possible the order of increasing base strength is: \(LiH

Numerical Problems

1. Arrange these acids in order of increasing strength.
   - acid A: $pK_a = 1.52$
   - acid B: $pK_a = 6.93$
   - acid C: $pK_a = 3.86$

Given solutions with the same initial concentration of each acid, which would have the highest percent ionization?

2. Arrange these bases in order of increasing strength:
   - base A: $pK_b = 13.10$
   - base B: $pK_b = 8.74$
   - base C: $pK_b = 11.87$

   Given solutions with the same initial concentration of each base, which would have the highest percent ionization?

3. Calculate the K_a and the pK_a of the conjugate acid of a base with each pK_b value.
   a. 3.80
   b. 7.90
   c. 13.70
   d. 1.40
   e. −2.50
4. Benzoic acid is a food preservative with a pK_a of 4.20. Determine the K_b and the pK_b for the benzoate ion.
5. Determine K_a and pK_a of boric acid $[B(OH)_3]$, solutions of which are occasionally used as an eyewash; the pK_b of its conjugate base is 4.80.

Numerical Answers

1. Acids in order of increasing strength: \(acid\,B

2. Bases in order of increasing strength: \(base\,A

3.

a.

$pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 3.80 = 10.2$

$K_a = 10^{-pK_a} = 10^{-10.2} = 6.31 \times 10^{-11}$

b.

$pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 7.90 = 6.10$

$K_a = 10^{-pK_a} = 10^{-6.10} = 7.94 \times 10^{-7}$

c.

$pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 7.90 = 3.000 \times 10^{-1}$

$K_a = 10^{-pK_a} = 10^{-3.000 \times 10^{-1}} = -5.012 \times 10^{-1}$

d.

$pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 1.40 = 12.6$

$K_a = 10^{-pK_a} = 10^{-12.6} = 2.51 \times 10^{-13}$

e. $pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 7.90 = 16.5$

$K_a = 10^{-pK_a} = 10^{-16.5} = 3.16 \times 10^{-17}$

4.

$pK_a + pK_b = 14 \rightarrow pK_b = 14 - pK_a = 14 - 4.20 = 9.80$

$K_b = 10^{-pK_b} = 10^{-9.80} = 1.58 \times 10^{-10}$

5.

$pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 4.80 = 9.20$

$K_a = 10^{-pK_a} = 10^{-9.20} = 6.31 \times 10^{-10}$

16.3: The Autoionization of Water

Conceptual Problems

1. What is the relationship between the value of the equilibrium constant for the autoionization of liquid water and the tabulated value of the ion-product constant of liquid water (K_w)?
2. The density of liquid water decreases as the temperature increases from 25°C to 50°C. Will this effect cause K_w to increase or decrease? Why?
3. Show that water is amphiprotic by writing balanced chemical equations for the reactions of water with HNO_3 and NH_3. In which reaction does water act as the acid? In which does it act as the base?
4. Write a chemical equation for each of the following.
   a. Nitric acid is added to water.
   b. Potassium hydroxide is added to water.
   c. Calcium hydroxide is added to water.
   d. Sulfuric acid is added to water.
5. Show that K for the sum of the following reactions is equal to K_w.

$$HMnO_4\,(aq) \rightleftharpoons H^+\,(aq) + MnO_4^-\,(aq) \tag{16.E.1}$$

$$MnO_4^-\,(aq) + H_2O\,(l) \rightarrow HMnO_4\,(aq) + OH^-\,(aq) \tag{16.E.2}$$

Conceptual Answers

1.

$$K_{auto} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \tag{16.E.3}$$

$$K_w = [H_3O^+][OH^-] = K_{auto}[H_2O]^2 \tag{16.E.4}$$

2. This will affect K_w as it is dependent on temperature. As the temperature increases, an endothermic process occurs (energy must be absorbed to break the bonds). Consequently, according to Le Chatelier, an increase in temperature favors the forward reaction thus the position of equilibrium shifts toward the right-hand side and K_w becomes larger.

3.
Water acts as the base:

$$H_2O\,(l) + HNO_3\,(g) \rightarrow H_3O^+\,(aq) + NO_3^-\,(aq) \tag{16.E.5}$$

Water acts as the acid:

$$H_2O\,(l) + NH_3\,(g) \rightarrow OH^-\,(aq) + NH_4^-\,(aq) \tag{16.E.6}$$

4.

a. $HNO_3\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + HNO_2^-\ (aq)$

b. $KOH\ (s) + H_2O\ (l) \rightleftharpoons K^-\ (aq) + OH^-\ (aq)$

c. $Ca(OH)_2\ (s) + H_2O\ (l) \rightleftharpoons Ca^{2+}\ (aq) + 2\ OH^-\ (aq)$

d. $H_2SO_4\ (aq) + H_2O\ (l) \rightleftharpoons HSO_4^-\ (aq) + H^+\ (aq)$

5.

$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$

$K_w = [H^+][OH^-]$

Numerical Problems

1. The autoionization of sulfuric acid can be described by the following chemical equation:

$$H_2SO_4\,(l) + H_2SO_4\,(aq) \rightleftharpoons H_3SO_4^+\,(aq) + HSO_4^-\,(aq) \tag{16.E.7}$$

   At 25°C, $K = 3 \times 10^{-4}$. Write an equilibrium constant expression for $K_{H_2SO_4}$ that is analogous to K_w. The density of H_2SO_4 is $1.8\frac{g}{cm^3}$ at 25°C. What is the concentration of $H_3SO_4^+$? What fraction of H_2SO_4 is ionized?
2. An aqueous solution of a substance is found to have $[H_3O]^+ = 2.48 \times 10^{-8}\ M$. Is the solution acidic, neutral, or basic?
3. The pH of a solution is 5.63. What is its pOH? What is the $[OH^-]$? Is the solution acidic or basic?
4. State whether each solution is acidic, neutral, or basic.
   a. $[H_3O^+] = 8.6 \times 10^{-3}\ M$
   b. $[H_3O^+] = 3.7 \times 10^{-9}\ M$
   c. $[H_3O^+] = 2.1 \times 10^{-7}\ M$
   d. $[H_3O^+] = 1.4 \times 10^{-6}\ M$
5. Calculate the pH and the pOH of each solution.
   a. 0.15 $M\ HBr$
   b. 0.03 $M\ KOH$
   c. $2.3 \times 10^{-3}\ M\ HNO_3$
   d. $9.78 \times 10^{-2}\ M\ NaOH$
   e. 0.00017 $M\ HCl$
   f. 5.78 $M\ HI$
6. Calculate the pH and the pOH of each solution.
   a. 25.0 mL of $2.3 \times 10^{-2}\ M\ HCl$, diluted to 100 mL
   b. 5.0 mL of $1.87\ M\ NaOH$, diluted to 125 mL
   c. 5.0 mL of $5.98\ M\ HCl$ added to 100 mL of water
   d. 25.0 mL of $3.7\ M\ HNO_3$ added to 250 mL of water
   e. 35.0 mL of $0.046\ M\ HI$ added to 500 mL of water
   f. 15.0 mL of $0.0087\ M\ KOH$ added to 250 mL of water.
7. The pH of stomach acid is approximately 1.5. What is the $[H^+]$?
8. Given the pH values in parentheses, what is the $[H^+]$ of each solution?
   a. household bleach (11.4)
   b. milk (6.5)
   c. orange juice (3.5)
   d. seawater (8.5)
   e. tomato juice (4.2)
9. A reaction requires the addition of 250.0 mL of a solution with a pH of 3.50. What mass of HCl (in milligrams) must be dissolved in 250 mL of water to produce a solution with this pH?
10. If you require 333 mL of a pH 12.50 solution, how would you prepare it using a 0.500 M sodium hydroxide stock solution?

Numerical Answers

1.

$$K_{H_2SO_4} = [H_3SO_4^+][HSO_4^-] = K[H_2SO_4]_2 \tag{16.E.8}$$

$$[H_3SO_4^+] = 0.3\,M \tag{16.E.9}$$

So the fraction ionized is 0.02.

2. The solution is basic because the $pH = -log([H_3O^+]) = -log(2.48 \times 10^{-8}) = 7.61 > 7$.

3.

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 5.63 = 8.37$

$[OH^-] = 10^{-pOH} = -4.27 \times 10^{-9}$

The $pH = 5.63 < 7$, therefore the solution is acidic.

4.

a. The solution is acidic. $pH = -log([H_3O^+]) = -log(8.6 \times 10^{-3}) = 2.1 < 7$

b. The solution is basic. $pH = -log([H_3O^+]) = -log(3.7 \times 10^{-9}) = 8.4 > 7$

c. The solution is acidic. $pH = -log([H_3O^+]) = -log(2.1 \times 10^{-7}) = 6.7 < 7$

d. The solution is acidic. $pH = -log([H_3O^+]) = -log(1.4 \times 10^{-6}) = 5.9 < 7$

5.

a.

$pH = -log([H_3O^+]) = -log(0.15) = 0.82$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 0.82 = 13$

b.

$pOH = -log([OH^-]) = -log(0.03) = 2$

$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 2 = 10$

c.

$pH = -log([H_3O^+]) = -log(2.3 \times 10^{-3}) = 2.6$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 2.6 = 11$

d.

$pOH = -log([OH^-]) = -log(9.78 \times 10^{-2}) = 1.01$

$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 1.01 = 13.0$

e.

$pH = -log([H_3O^+]) = -log(0.00017) = 3.8$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 3.8 = 10$

f.

$pH = -log([H_3O^+]) = -log(5.78) = -0.762$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - (-0.762) = 14.8$

6.

a. $25.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{2.3 \times 10^{-2}\ mol}{1\ L} \times \frac{1}{100\ mL \times \frac{1\ L}{1{,}000\ mL}} = 0.060\ M\ HCl$

$pH = -log([H_3O^+]) = -log(0.060) = 1.22$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 1.22 = 12.78$

b. $5.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{1.87\ mol}{1\ L} \times \frac{1}{125\ mL \times \frac{1\ L}{1{,}000\ mL}} = 7.5 \times 10^{-2}\ M\ NaOH$

$pOH = -log([OH^-]) = -log(7.5 \times 10^{-2}) = 1.1$

$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 1.1 = 12.9$

c. $5.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{5.98\ mol}{1\ L} \times \frac{1}{100\ mL \times \frac{1\ L}{1{,}000\ mL}} = 0.20\ M\ HCl$

$pH = -log([H_3O^+]) = -log(0.20) = 0.70$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 0.70 = 13.3$

d. $25.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{3.7\ mol}{1\ L} \times \frac{1}{250\ mL \times \frac{1\ L}{1{,}000\ mL}} = 0.370\ M\ HNO_3$

$pH = -log([H_3O^+]) = -log(0.370) = 0.432$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 0.432 = 13.568$

e. $35.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{0.046\ mol}{1\ L} \times \frac{1}{500\ mL \times \frac{1\ L}{1{,}000\ mL}} = 3 \times 10^{-3}\ M\ HI$

$pH = -log([H_3O^+]) = -log(3 \times 10^{-3}) = 2.52$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 2.52 = 11.48$

f. $15.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{0.0087\ mol}{1\ L} \times \frac{1}{125\ mL \times \frac{1\ L}{1{,}000\ mL}} = 5.20 \times 10^{-4}\ M\ KOH$

$pOH = -log([OH^-]) = -log(5.20 \times 10^{-4}) = 3.28$

$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 3.28 = 10.72$

7. $[H^+] = 10^{-pH} = 10^{-1.5} = 3.2 \times 10^{-2}\ M$

8.

a. $[H^+] = 10^{-11.4} = 3.98 \times 10^{-12}\ M$

b. $[H^+] = 10^{-6.5} = 3.2 \times 10^{-7}\ M$

c. $[H^+] = 10^{-3.5} = 3.2 \times 10^{-4}\ M$

d. $[H^+] = 10^{-8.5} = 3.2 \times 10^{-9}\ M$

e. $[H^+] = 10^{-4.2} = 6.3 \times 10^{-5}\ M$

9. 2.9 mg HCl

$[H^+] = 10^{-pH} = 10^{-3.50} = 3.1622 \times 10^{-4}\ M$

$x\ mg\ HCl \times \frac{1\ g\ HCl}{1{,}000\ mg\ HCl} \times \frac{1\ mol\ HCl}{36.46\ g\ HCl} \times \frac{1}{250\ mL\ H_2O \times \frac{1\ L}{1{,}000\ mL\ H_2O}} = 3.1622 \times 10^{-4}\ M\ HCl \rightarrow \frac{x\ mol\ HCl}{9115\ L\ HCl} = 3.1622 \times 10^{-4}\ M\ HCl \rightarrow x\ mol\ HCl = 3.1622 \times 10^{-4}\ M \times 9115\ L\ HCl \rightarrow x\ mol\ HCl = 2.9\ mol\ HCl \rightarrow x = 2.9$

10. To prepare the stock solution, $2.11 \times 10^{-2}\ L$ of $0.500\ M\ NaOH$ solution is required.

$\frac{0.03162\ mol\ NaOH}{1\ L\ NaOH} \times \frac{1\ L\ NaOH}{0.5\ mol\ NaOH} \times 0.333\ L = 2.11 \times 10^{-2}\ g\ NaOH.$

$[OH^-] = 10^{-1.5} = 0.03162\ M$

$pH + pOH = 14 \rightarrow pOH = 14 - 12.50 = 1.5$

16.4: The pH Scale

16.5: Strong Acids and Bases

16.6: Weak Acids

16.7: Weak Bases

16.8: Relationship Between Ka and Kb

16.9: Acid-Base Properties of Salt Solutions

16.10: Acid-Base Behavior and Chemical Structure

Conceptual Problems

1. Several factors affect the relative strengths of acids and bases. For each pair, identify the most important factor in determining which is the stronger acid or base in aqueous solution.
   a. $CH_3CCl_2CH_2CO_2H$ versus $CH_3CH_2CH_2CO_2H$
   b. CH_3CO_2H versus CH_3CH_2OH
   c. $HClO$ versus $HBrO$
   d. $\mathrm{CH_3C(=O)NH_2}$ versus $CH_3CH_2NH_2$
   e. H_3AsO_4 versus H_3AsO_3
2. The stability of the conjugate base is an important factor in determining the strength of an acid. Which would you expect to be the stronger acid in aqueous solution—$C_6H_5NH_3^+$ or NH_4^+? Justify your reasoning.
3. Explain why H_2Se is a weaker acid than HBr.
4. Arrange the following in order of decreasing acid strength in aqueous solution: H_3PO_4, $CH_3PO_3H_2$, and $HClO_3$.
5. Arrange the following in order of increasing base strength in aqueous solution: $\mathrm{CH_3S^-}$, OH^-, and CF_3S^-.
6. Arrange the following in order of increasing acid strength in aqueous solution: $HClO_2$, HNO_2, and HNO_3.
7. Do you expect H_2SO_3 or H_2SeO_3 to be the stronger acid? Why?
8. Give a plausible explanation for why CF_3OH is a stronger acid than CH_3OH in aqueous solution. Do you expect $CHCl_2CH_2OH$ to be a stronger or a weaker acid than CH_3OH? Why?
9. Do you expect Cl_2NH or NH_3 to be the stronger base in aqueous solution? Why?

Conceptual Answers

1.

a. The most important factor in determining the stronger acid is considering the inductive effect. Chlorine is an electron-withdrawing group. It pulls electron density away from the compound by means of the inductive effect through the sigma bond. In considering the conjugate base of $CH_3CCl_2CH_2CO_2H$, Chlorine absorbs some of the electron density or excess negative charge on the oxygen atom. This causes the C bonded to the attached Chlorine atoms to be partially positive. The conjugate base of $CH_3CCl_2CH_2CO_2H$ is more stable, thus more acidic than the conjugate base of $CH_3CH_2CH_2CO_2H$.

b. The most important factor in determining the stronger acid is knowing the pK_a values for functional groups. The pK_a of alcohol is about 16 while the pK_a of a carboxylic acid is about 5. Therefore, CH_3CO_2H is more acidic than CH_3CH_2OH.

c. The most important factor in determining the stronger acid is electronegativity. The chlorine atom is more electronegative than the bromine atom, therefore $HClO$ is more acidic than $HBrO$.

d. The most important factor in determining the stronger acid is considering resonance. The $\mathrm{CH_3C(=O)NH_2}$ has a resonance

which increases the stability of the conjugate base (therefore increasing acidity) because the negative charge can be delocalized. Thus, $\mathrm{CH_3C(=O)NH_2}$ is more acidic than $CH_3CH_2NH_2$.

e. The most important factor in determining the stronger acid is considering oxidation states on the central nonmetal. H_3AsO_4 has an oxidation state of +5 which is larger and thus more acidic than H_3AsO_3 which has an oxidation state of +3.

$CF_3S^- < CH_3S^- < OH^-$ (strongest base)

NH_3; Cl atoms withdraw electron density from N in Cl_2NH.

2. It is expected that the stronger acid is $C_6H_5NH_3^+$ because in considering the conjugate base the lone pair of electrons on nitrogen is involved in resonance, hence the molecule is stable.

3. H_2Se is a weaker acid than HBr because Br is more electronegative than Se thus more stable.

4. $HClO_3 > CH_3PO_3H_2 > H_3PO_4$

This is because H_3PO_4 is a polyprotic acid which contains more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus, acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases which indicate it is the most basic. The conjugate base of ClO^{3-} has a much smaller charge to volume ratio, thus most stable and acidic.

5. \(CF_{3}S^{-}

CF_3S^- is the most acidic because of the three electronegative Fluorines. OH^- is the strongest base in water. Thus, CH_3S^- is in between these aqueous solutions.

6. \(HNO_2

HNO_3 has resonance stabilization, therefore it is the most acidic. Between $HClO_2$ and HNO_2, Cl is the most electronegative therefore $HClO_2$ is more acidic than HNO_2.

7. I expect H_2SO_3 to be the stronger acid because it is more electronegative or has greater attraction which means it'll be less inclined to share their electrons with a proton.

8. CF_3OH is a stronger acid than CH_3OH in aqueous solution because F is more electronegative than H.

9. It would be expected that NH_3 be a stronger base than Cl_2NH because it is electronegative due to the two Cl atoms.

16.11: Lewis Acids and Bases

Problems

1. Identify the nature of each of the following as either a Lewis Acid or a Lewis Base:

a. NH_3
b. Ag^+
c. Ni^{2+}
d. Pt^{4+}
e. H_2O
f. SO_2

2. Explain why SiF_4 can act as a Lewis Acid.

3. Identify the nature of each of the following as either a Lewis Acid or a Lewis Base:

a. $[Fe(CN)_6]^{3-}$

b. $[Ni(NH_3)_6]^{2+}$
c. $CdBr_4^{2-}$

4. What is the product of the reaction of $CO_2 + OH^- \rightarrow$?

5. In the reactions below, which is the Lewis Acid and/or which is the Lewis Base?

a. $NH_3 + H^+ \rightarrow NH_4^+$
b. $H_2O + H^+ \rightarrow H_3O^+$

6. In the complex ion, $[PtCl_6]^{2-}$ which is the Lewis Acid and which is the Lewis base?

7. The reaction of $AgCl$ + NH_3 produces what complex ion?

Solutions

1.

a. NH_3 is a lewis base because nitrogen has a lone pair of electrons to "donate."

b. Ag^+ is a lewis acid because it has an unfilled octet and thus is able to accept a pair of electrons.

c. Ni^+ is a lewis acid because it has an unfilled octet and thus is able to accept a pair of electrons.

d. Pt^{4+} is a lewis acid because it has an unfilled octet and thus is able to accept a pair of electrons.

e. H_2O is a lewis base because oxygen has two lone pairs of electrons to "donate."

f. SO_2 is a lewis acid because sulfur has an unfilled octet and thus is able to accept a pair of electrons.

2. \(SiF_4\) has a central Silicon Atom which can expand its octet to 12 (compared to the typical 8) so that it forms \([SiF_6]^{2-}\).

3.

a. Lewis Acid: Fe^{3+}, Lewis Base: CN^-
b. Lewis Acid: Ni^{2+}, Lewis Base: NH_3
c. Lewis Acid: Cd^{2+}, Lewis Base: Br^-

4. This reaction forms a bicarbonate ion. $CO_2 + OH^- \rightarrow O--COH=O$.

5.

a. Lewis Acid: H^+, Lewis Base: NH_3

b. Lewis Acid: H^+, Lewis Base: H_2O

6. Pt^{4+} is the Lewis acid and Cl^- is the Lewis base.

7.

$$AgCl + 2\,NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^- \tag{16.E.10}$$

Conceptual Problems

1. Construct a table comparing how OH^-, NH_3, H_2O, and BCl_3 are classified according to the Arrhenius, the Brønsted–Lowry, and the Lewis definitions of acids and bases

2. Describe how the proton (H^+) can simultaneously behave as an Arrhenius acid, a Brønsted–Lowry acid, and a Lewis acid.

3. Would you expect aluminum to form compounds with covalent bonds or coordinate covalent bonds? Explain your answer.

4. Classify each compound as a Lewis acid or a Lewis base and justify your choice.

   a. $AlCl_3$

   b. CH_3N

   c. IO_3^-

5. Explain how a carboxylate ion (RCO_2^-) can act as both a Brønsted–Lowry base and a Lewis base.

Conceptual Answers

1.

	Arrhenius Acid	Arrhenius Base	Brønsted–Lowry Acid	Brønsted–Lowry Base	Lewis Acid	Lewis Base
OH^-		X		X		X
NH_3				X		X
H_2O	X	X	X	X		X
BCl_3					X	

An Arrhenius acid is a molecule that when dissolved in water it will donate an H^+ in solution.

An Arrhenius base is a molecule that when dissolved in water it will donate an OH^- in solution.

A Brønsted–Lowry acid is a molecule that when dissolved in a solution it will donate an H^+ in solution.

A Brønsted–Lowry base is a molecule that when dissolved in a solution it will donate an atom or ion capable of accepting or bonding to a free proton in solution.

A Lewis acid is an atom or molecule that accepts an electron pair.

A Lewis base is an atom or molecule that donates an electron pair.

2.

The proton (H^+) can simultaneously behave as an Arrhenius acid because when it is dissolved in water it will donate itself. $H^+ + H_2O \rightleftharpoons H_3O^+$

The proton (H^+) can simultaneously behave as a Brønsted–Lowry acid because when it is dissolved in solution it will donate itself.

$H^+ + B^- \rightleftharpoons HB$

The proton (H^+) can simultaneously behave as a Lewis acid as it can accept an electron pair.

$H^+ + B^- \rightleftharpoons HB$

3. It is expected that Aluminum forms a coordinate covalent bond as it can participate in a Lewis acid and a Lewis base interaction. For example $Al^{3+} + H_2O \rightleftharpoons [Al(OH_2)_6]^{3+}$

4.

a. $AlCl_3$ is a Lewis acid as Al can accept an electron pair.

b. CH_3N is a Lewis base as N can donate an electron pair.

c. IO_3^- is a Lewis base as I can donate an electron pair.

5. The carboxylate ion (RCO_2^-) can act as Brønsted–Lowry base because when dissolved in a solution the electron rich O is capable of accepting a proton. The carboxylate ion (RCO_2^-) can act as a Lewis base because the electron rich O can donate an electron pair.

Numerical Problems

1. In each reaction, identify the Lewis acid and the Lewis base and complete the reaction by writing the products(s).

a. $(CH_3)_2O + AlCl_3$

b. $SnCl_4 + 2\ Cl^-$

2. Use Lewis dot symbols to depict the reaction of BCl_3 with dimethyl ether [$(CH_3)_2O$]. How is this reaction similar to that in which a proton is added to ammonia?

Answer

1.

a. The Lewis acid is $AlCl_3$ and the Lewis base is $(CH_3)_2O$.

$$(CH_3)_2O + AlCl_3 \rightleftharpoons AlCl_3 \cdot O(CH_3)_2$$

b. The Lewis acid is $SnCl_4$ and the Lewis base is Cl^-.

$$SnCl_4 + 2\ Cl^- \rightleftharpoons SnCl_6^{2-}$$

2.

$$BCl_3 + (CH_3)_2O \rightleftharpoons BCl_3 \cdot O(CH_3)_2$$

This reaction is similar to that in which a proton is added to ammonia as it also involves a Lewis acid and a Lewis base interaction.

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16.S: Acid–Base Equilibria (Summary)

16.1: Acids and Bases: A Brief Review

- acids have sour taste and turn litmus paper red
- bases have a bitter taste and feel slippery
- Svante Arrhenius (1859-1927)
- Acids associated with H^+ ions
- Bases associated with OH^- ions
- Solution is acidic if $[H^+] > [OH^-]$
- Solution is basic if $[OH^-] > [H^+]$

16.2: Brønsted–Lowry Acids and Bases

- Arrhenius definition of acids and bases
  - Acids when dissolved in water increase H^+ concentration
  - Bases when dissolved in water increase OH^- concentration

16.2.1 Proton Transfer Reactions

- Brønsted-Lowry definition of acids an bases
- Acid is a proton donor
- Base is a proton acceptor
- Can be applied to non-aqueous solutions
- Brønsted-Lowry acid must be able to lose a H^+ ion
- Brønsted-Lowry base must have at least one non-bonding pair (lone pair) of electrons to bind to H^+ ion
- Amphoteric - substance that can act as an acid or base

16.2.2 Conjugate Acid-Base Pairs

- conjugate acid - product formed by adding a proton to base
- conjugate base - product formed by removal of a proton from acid

16.2.3 Related Strengths of Acids and Bases

- the stronger the acid, the weaker the conjugate base
- the stronger the base, the weaker the conjugate acid
- equilibrium favors transfer of proton from stronger acid to stronger base

16.3: The Autoionization of Water

- autoionization of water - dissociation of H_2O molecules to H^+ and OH^- ions
- at room temperature only 1 out of 10^9 molecules are ionized
- exclude water from equilibrium expressions involving aqueous solutions
- ion-product constant
- $k_w = k[H_2O] = [H^+][OH^-] = 1.0 \times 10^{-14}$ (at 25° C)
- solution is neutral when $[H^+] = [OH^-]$
- solution is acidic when $[H^+] > [OH^-]$

- solution is basic when $[H^+] < [OH^-]$

16.3.1 The Proton in Water

- H^+ ion is a proton with no valence electrons
- H^+ ion react with H_2O molecule to form H_3O^+, hydronium ion
- H_3O^+ ion can bond with other H_2O molecules to form hydrated hydrogen ions
- H^+ and H_3O^+ used interchangeably

16.4: The pH Scale

- concentration of $[H^+]$ expressed in terms of pH
- pH = -log $[H^+]$
- acidic solutions $[H^+] > 1.0 \times 10^{-7}$ $[OH^-] < 1.0 \times 10^{-7}$ pH < 7.00
- neutral solutions $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ pH = 7
- basic solutions $[H^+] < 1.0 \times 10^{-7}$ $[OH^-] > 1.0 \times 10^{-7}$ pH > 7

Other "p" Series

- pOH = -log $[OH^-]$
- pH + pOH = -log K_w = 14.00

Measuring pH

- pH meter
  - has a pair of electrodes connected to a meter that measures in millivolts
  - voltage generated when electrodes placed in solution, and is measured by meter
- blue litmus paper turns red in acidic solution
- red litmus paper turns blue in basic solution

16.5: Strong Acids and Bases

strong acids and bases are strong electrolytes

16.5.1 Strong Acids

strongest monoprotic acids

- HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, and diprotic H_2SO_4
- For strong monoprotic acid concentration of $[H^+]$ equals the original concentration of the acid

16.5.2 Strong Bases

- most common strong bases are ionic hydroxides of alkali metals and the heavier alkaline-earth metals
- complete dissociation

16.6: Weak Acids

- $HA_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+ + A^-_{(aq)}$
- $HA_{(aq)} \rightarrow H^+_{(aq)} + A^-_{(aq)}$
- $K_a = \frac{[H^+][A^-]}{[HA]}$

- K_a = acid - dissociation constant
- The lager the K_a the stronger the acid
- K_a usually less than 10^{-3}

16.6.1 Calculating pH for Solutions of Weak Acids

- 1) write ionization equilibrium
- 2) write equilibrium expression
- 3) I.C.E. Table
- 4) substitute equilibrium concentrations into equilibrium expression
  - percent ionization = fraction of weak acid molecules that ionize * 100%
  - in weak acids $[H^+]$ is small fraction of concentration of acid
  - percent ionization depends on temperature, identity of acid and concentration
  - as percent ionization decreases, concentration increases

16.6.2 Polyprotic Acids

- more than one ionizable H atom
- easier to remove first proton than second
- acid dissociation constants are K_{a1}, K_{a2}, etc...
- K_a values usually differ by 10^3

16.7: Weak Bases

- base-dissociation constant, K_b
- equilibrium at which base reacts with H_2O to form a conjugate acid and OH^-
- contain 1 or more lone pair of electrons

16.7.1 Types of Weak Bases

- weak bases have NH_3 and anions of weak acids

16.8: Relationship Between K_a and K_b

- when two reactions are added together then equilibrium constant of third reaction is equal to the product of the equilibrium constants of the added reactions
- reaction 1 + reaction 2 = reaction 3
- $K_1 \times K_2 = K_3$
- $K_a \times K_b = [H^+][OH^-] = K_w$
- Acid-dissociation constant times base-dissociation constant equals the ion-product constant for water
- $K_a \times K_b = K_w = 1.0 \times 10^{-14}$
- $pK_a \times pK_b = pK_w = 14$; ($pK_a$= -log K_a and pK_b = -log K_b)

16.9: Acid-Base Properties of Salt Solutions

- hydrolysis - ions reacting with water to produce H^+ and OH^- ions
- anions from weak acids react with water to produce OH^- ions which is basic
- anions of strong acids are not basic and do not influence pH
- anions that have ionizable protons are amphoteric
- behavior depends on K_a and K_b
- all cations except those of alkali metals and heavier alkaline earth (Ca^{2+}, Sr^{2+} and Ba^{2+}) are weak acids in water

- alkali metal and alkaline earth cations do not hydrolyze
- do not affect pH
- strengths of acids and bases from salts
- 1) salts derived from strong acid and base
  - no hydrolysis and solution has pH of 7
- 2) salts derived from strong base and weak acid
  - strong conjugate base
  - anion hydrolyzes and produces OH^- ions
  - cation does not hydrolyze
  - pH greater than 7
- 3) salts derived from weak base and strong acids
  - cation is strong conjugate acid
  - cation hydrolyzes to produce H^+
  - anion does not hydrolyze
  - solution has pH below 7
- 4) salts derived from weak acid and base
  - both cation and anion hydrolyze
  - pH depends on extent on hydrolysis of each ion]

16.10: Acid-Base Behavior and Chemical Structure

16.10.1 Factors that Affect Acid Strength

- strength of acid depends on:
  - 1) polarity of H-X bond
  - 2) strength of H-X bond
  - 3) stability of conjugate base, X^-
- molecule will transfer proton if H-X bond is polarized
- in ionic hydrides H^- acts as proton acceptor because of negative charge
- nonpolar bonds produce neither acidic nor basic solutions
- strong bonds less easily dissociated that weak bonds
- the greater the stability of conjugate base, the stronger the acid]

16.10.2 Binary Hydrides

- metal hydrides are basic or have no acid-base properties in water
- nonmetal hydrides can be between having no acid-base properties to being acidic
- in each group of nonmetallic elements, acidity increases with increasing atomic number
  - bond strengths decrease as central atom gets larger and overlap of orbitals get smaller

16.10.3 Oxyacids

- Y-O-H bond
- Oxyacids - have OH bonded to central atom
- Base if bonded to a metal because pair of electrons shared between Y-O is completely transferred to O
  - Ionic compound with OH^- is formed
- When bonded to nonmetal the bond is covalent and compounds are acidic or neutral
- As electronegativity of Y increases , acidity also increases
  - O-H bond becomes more polar
  - Conjugate base usually an anion and stability increases as electronegativity of Y increases
- Relating acid strengths of oxyacids to electronegativity of Y and to number of groups attached to Y
  - 1) same number of oxygen atoms, acid strength increases as electronegativity of central atom increases
  - 2) same central atom Y, acid strength increases with increasing number of bonded oxygen atoms to central atom
    - acidity increases as oxidation number of central atom increases

16.10.4 Carboxylic Acids

- carboxyl group - COOH
- acidic behavior of carboxylic acids
  - addition oxygen atom in carboxyl group draws density from O-H bond which increases the polarity
  - conjugate base ion have resonance forms
  - acidity increases as number of electronegative atoms in acid increases

16.11: Lewis Acids and Bases

- Lewis acid - electron pair acceptor
- Lewis base - electron pair donor
- Any Brønsted-Lowry base is a Lewis base
- Lewis acids contain at least one atom with an incomplete octet

16.11.1 Hydrolysis of Metal Ions

- hydration - attraction of metal ions to water molecules
  - metal ion acts as Lewis acid
  - water molecule acts as Lewis base
  - electron density drawn from oxygen atom to water molecule
  - O-H bond becomes more polarized
- For hydrolysis reactions K_a increases with increasing charge and decreasing radius of ion

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17: ADDITIONAL ASPECTS OF AQUEOUS EQUILIBRIA

This chapter address equilibria with solutions containing more than one solute.

17.1: The Common-Ion Effect

17.2: Buffered Solutions

17.3: Acid-Base Titrations

17.4: Solubility Equilibria

17.5: Factors that Affect Solubility

17.6: Precipitation and Separation of Ions

17.7: Qualitative Analysis for Metallic Elements

17.E: Additional Aspects of Aqueous Equilibria (Exercises)

17.S: Additional Aspects of Aqueous Equilibria (Summary)

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17.1: The Common-Ion Effect

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common-ion effect is used to describe the effect on an equilibrium involving a substance that adds an ion that is a part of the equilibrium.

Introduction

The solubility products K_{sp}'s are equilibrium constants in heterogeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[\mathrm{Na}^+] + [\mathrm{K}^+] = [\mathrm{Cl}^-] \tag{17.1.1}$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion.

Common Ions

When NaCl and KCl are dissolved in the same solution, the Cl^- ions are *common* to both salts. In a system containing NaCl and KCl, the Cl^- ions are common ions.

$$\mathrm{NaCl} \rightleftharpoons \mathrm{Na}^+ + \mathrm{Cl}^-$$

$$\mathrm{KCl} \rightleftharpoons \mathrm{K}^+ + \mathrm{Cl}^-$$

$$\mathrm{CaCl_2} \rightleftharpoons \mathrm{Ca}^{2+} + 2\mathrm{Cl}^-$$

$$\mathrm{AlCl_3} \rightleftharpoons \mathrm{Al}^{3+} + 3\mathrm{Cl}^-$$

$$\mathrm{AgCl} \rightleftharpoons \mathrm{Ag}^+ + \mathrm{Cl}^-$$

For example, when AgCl is dissolved into a solution already containing NaCl (actually Na^+ and Cl^- ions), the Cl^- ions come from the ionization of both AgCl and NaCl. Thus, $[\mathrm{Cl}^-]$ differs from $[\mathrm{Ag}^+]$. The following examples show how the concentration of the common ion is calculated.

Example 17.1.1

What are $[\mathrm{Na}^+]$, $[\mathrm{Cl}^-]$, $[\mathrm{Ca}^{2+}]$, and $[\mathrm{H}^+]$ in a solution containing 0.10 M each of NaCl, $\mathrm{CaCl_2}$, and HCl?

Solution

Due to the conservation of ions, we have

$$[\mathrm{Na}^+] = [\mathrm{Ca}^{2+}] = [\mathrm{H}^+] = 0.10\ \mathrm{M}$$

but

$$\begin{aligned}[\mathrm{Cl}^-] = &\ 0.10\ (\text{due to NaCl}) \\ &+ 0.20\ (\text{due to } \mathrm{CaCl_2}) \\ &+ 0.10\ (\text{due to HCl}) \\ = &\ 0.40\ \mathrm{M}\end{aligned}$$

Exercise 17.1.1

John poured 10.0 mL of 0.10 M NaCl, 10.0 mL of 0.10 M KOH, and 5.0 mL of 0.20 M HCl solutions together and then he made the total volume to be 100.0 mL. What is $[\mathrm{Cl}^-]$ in the final solution?

Solution

$$[\mathrm{Cl}^-] = \frac{0.1\ \mathrm{M} \times 10\ \mathrm{mL} + 0.2\ \mathrm{M} \times 5.0\ \mathrm{mL}}{100.0\ \mathrm{mL}} = 0.020\ \mathrm{M}$$

Le Châtelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

Example 17.1.2: Solubility of Lead Chloride

Consider the lead(II) ion concentration in this *saturated* solution of $PbCl_2$. The balanced reaction is

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Defining s as the concentration of dissolved lead(II) chloride, then:

$$[Pb^{2+}] = s$$

$$[Cl^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s:

$$K_{sp} = [Pb^{2+}][Cl^-]^2 \tag{17.1.2}$$
$$= s \times (2s)^2 \tag{17.1.3}$$
$$1.7 \times 10^{-5} = 4s^3 \tag{17.1.4}$$
$$s^3 = \frac{1.7 \times 10^{-5}}{4} \tag{17.1.5}$$
$$= 4.25 \times 10^{-6} \tag{17.1.6}$$
$$s = \sqrt[3]{4.25 \times 10^{-6}} \tag{17.1.7}$$
$$= 1.62 \times 10^{-2}\ mol\ dm^{-3} \tag{17.1.8}$$

The concentration of lead(II) ions in the solution is 1.62 x 10^{-2} M. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression again:

$$PbCl_2\ (s) \rightleftharpoons Pb^{2+}\ (aq) + 2Cl^-\ (aq)$$

What happens to that equilibrium if extra chloride ions are added? According to *Le Châtelier*, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

Example 17.1.3

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[Pb^{2+}] = s \tag{17.1.9}$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution.

In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[Cl^{-}] = 0.100\ M \tag{17.1.10}$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^{-}]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.00100 \end{aligned}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3}\ \mathrm{M} \end{aligned} \tag{17.1.11}$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[Pb^{2+}] = 0.0162\ M \tag{17.1.12}$$

Solution in 0.100 M NaCl solution:

$$[Pb^{2+}] = 0.0017\ M \tag{17.1.13}$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.

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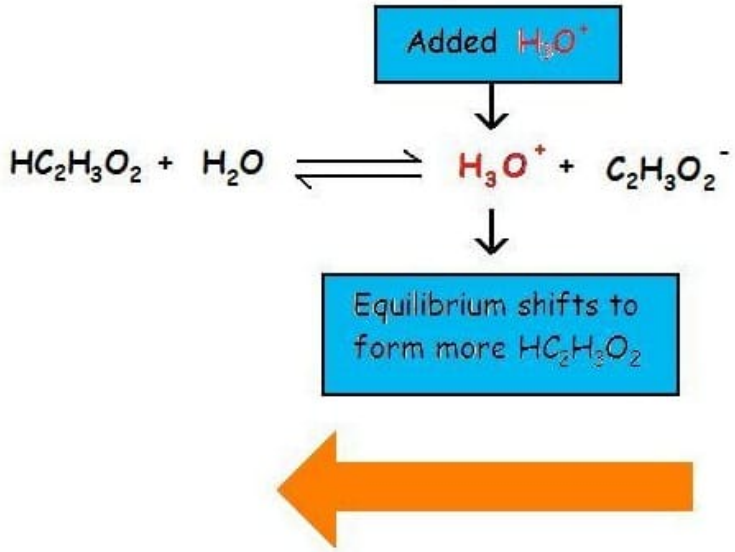
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Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.

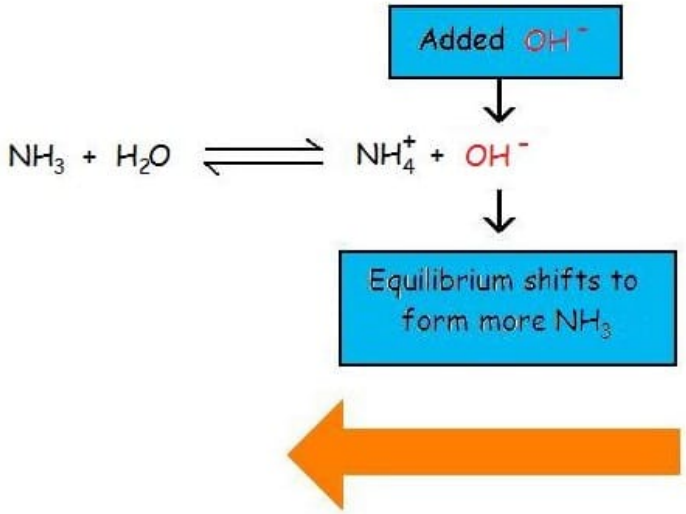
The common ion effect of H_3O^+ on the ionization of acetic acid



HC2H3O2 reactions with H2O to produce H3O plus and C2H3 O2 minus. If more H3O plus is added to the reaction, the equilibrium would shift to form more HC2H3O2.

When a strong acid supplies the common ion $\mathrm{H_3O^+}$ the equilibrium shifts to form more $\mathrm{HC_2H_3O_2}$.

The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium. Now consider the common ion effect of $\mathrm{OH^-}$ on the ionization of ammonia



When a strong base supplies the common ion $\mathrm{OH^-}$ the equilibrium shifts to form more $\mathrm{NH_3}$.
NH3 reacts with H2 O to produce NH4 plus and OH minus. If more OH minus is added to the reaction, the equilibrium would shifts to form more NH3.

Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with Le Chatelier's Principle), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[\mathrm{NH_4}^+][\mathrm{OH}^-]}{[\mathrm{NH_3}]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K.

Common Ion Effect on Solubility

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$\mathrm{Ca_3(PO_4)_2\,(s)} \rightleftharpoons 3\,\mathrm{Ca^{2+}\,(aq)} + 2\,\mathrm{PO_4^{3-}\,(aq)} \tag{17.1.14}$$

As you will discover in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate. The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2}{[\mathrm{Ca_3(PO_4)_2}]} \tag{17.1.15}$$

$$[\mathrm{Ca_3(PO_4)_2}]K = K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2 \tag{17.1.16}$$

At 25°C and pH 7.00, K_{sp} for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts vary dramatically for different compounds (Table E3). Although K_{sp} is not a function of pH in Equation 17.1.15, changes in pH can affect the solubility of a compound.

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. **Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions.** This dependency is another example of the common ion effect where adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains

- $3 \times (1.14 \times 10^{-7}\ M) = 3.42 \times 10^{-7} M\ \ of\ \ Ca^{2+}$
- $2 \times (1.14 \times 10^{-7} M) = 2.28 \times 10^{-7} M\ \ of\ \ PO_4^{3-}$

according to the stoichiometry shown in Equation 17.1.15 (neglecting hydrolysis to form HPO_4^{2-}). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that [Ca^{2+}] > 3.42×10^{-7} M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 17.1.15 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

Note

Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes the equilibrium to shift left, toward the reactants, causing precipitation.

Example 17.1.5

Consider the reaction:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$$

What happens to the solubility of $PbCl_2$(s) when 0.1 M NaCl is added?

Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: Cl^-

Notice: $Q_{sp} > K_{sp}$ The addition of NaCl has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of $PbCl_2$ is equivalent to the concentration of Pb^{2+} produced because they are in a 1:1 ratio.

Because K_{sp} for the reaction is 1.7×10^{-5}, the overall reaction would be $(s)(2s)^2 = 1.7 \times 10^{-5}$. Solving the equation for s gives s= 1.62×10^{-2} M. The coefficient on Cl^- is 2, so it is assumed that twice as much Cl^- is produced as Pb^{2+}, hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl^- added would be 0.1 M because Na^+ and Cl^- are in a 1:1 ration in the ionic salt, NaCl. Therefore, the overall molarity of Cl^- would be 2s + 0.1, with 2s referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$Q_{sp} = [Pb^{2+}][Cl^{-}]^2 \quad (17.1.17)$$
$$1.8 \times 10^{-5} = (s)(2s + 0.1)^2 \quad (17.1.18)$$
$$s = [Pb^{2+}] \quad (17.1.19)$$
$$= 1.8 \times 10^{-3} M \quad (17.1.20)$$
$$2s = [Cl^{-}] \quad (17.1.21)$$
$$\approx 0.1M \quad (17.1.22)$$

Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[Cl^-]$ is approximately 0.1M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for $PbCl_2$ is greater than the equilibrium constant because of the added Cl^-. This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

Exercise 17.1.5

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)

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A Video Discussing the Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products (opens in new window) [youtu.be]

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17.2: Buffered Solutions

Learning Objectives

- To understand how adding a common ion affects the position of an acid–base equilibrium.
- To know how to use the Henderson-Hasselbalch approximation to calculate the pH of a buffer.

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or "buffer," other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect: Weak Acids Combined with Conjugate Bases

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of H^+). Le Chatelier's principle can be used to predict the effect on the equilibrium position of the solution. A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. The dissociation reaction of acetic acid is as follows:

$$CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq) \tag{17.2.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3CO_2H]} \tag{17.2.2}$$

Sodium acetate (CH_3CO_2Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na^+ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier's principle predicts that the equilibrium in Equation 17.2.1 will shift to the left, consuming some of the added CH_3COO^- and some of the H^+ ions originally present in solution.

Because Na^+ is a **spectator ion**, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[H^+]$ is less than the initial value. Because $[H^+]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding any base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess H^+ ions react with the conjugate base ($CH_3CO_2^-$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower [$CH_3CO_2^-$] than before. In both cases, only the equilibrium composition has changed; the ionization constant K_a for acetic acid remains the same. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $CH_3CO_2^-$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is via the common ion effect.

Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.

Example 17.2.1

A 0.150 M solution of formic acid at 25°C (pKa = 3.75) has a pH of 2.28 and is 3.5% ionized.

a. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
b. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a, and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A. Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.
B. Substitute the expressions for the final concentrations into the expression for Ka. Calculate $[\mathrm{H}^+]$ and the pH of the solution.
C. Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

A Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:

$$\mathrm{HCO_2H\,(aq) \rightleftharpoons HCO_2^-\,(aq) + H^+\,(aq)}$$

The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

Final Concentration

ICE	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
Initial	0.150	1.00×10^{-7}	0.100
Change	–x	+x	+x
Equilibrium	(0.150 – x)	x	(0.100 + x)

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$\begin{aligned} K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} &= \frac{(x)(0.100 + x)}{0.150 - x} \\ &\approx \frac{x(0.100)}{0.150} \\ &\approx 10^{-3.75} \\ &\approx 1.8 \times 10^{-4} \end{aligned}$$

Rearranging and solving for x,

$$\begin{aligned} x &= (1.8 \times 10^{-4}) \times \frac{0.150\ M}{0.100\ M} \\ &= 2.7 \times 10^{-4} \\ &= [H^+] \end{aligned}$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover,

$$K_a C_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$$

which is greater than 1.0×10^{-6}, so again, our assumption is justified. The final pH is:

$$pH = -\log(2.7 \times 10^{-4}) = 3.57$$

compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Chatelier's principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

C Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$$HCO_2H(aq) \leftrightharpoons H^+(aq) + HCO_2^-(aq)$$

initial concentrations, changes in concentration, and final concentrations

	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
initial	0.150	0.200	0
change	–x	+x	+x
final	(0.150 – x)	(0.200 + x)	x

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[\mathrm{HCO_2}^-]$. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(0.200 + x)(x)}{0.150 - x} \approx \frac{x(0.200)}{0.150} = 1.80 \times 10^{-4}$$

Rearranging and solving for x,

$$x = (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M}$$
$$= 1.35 \times 10^{-4} = [HCO_2^-]$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4}\ M}{0.150\ M} \times 100\% = 0.0900\%$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding H^+ ions drives the dissociation equilibrium to the left.

Exercise 17.2.1

A 0.225 M solution of ethylamine ($\mathrm{CH_3CH_2NH_2}$ with $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

a. the pH of the solution if enough solid ethylamine hydrochloride ($\mathrm{EtNH_3Cl}$) is added to make the solution 0.100 M in $\mathrm{EtNH_3}^+$
b. the percentage of ethylamine that is ionized if enough solid NaOH is added to the original solution to give a final concentration of 0.050 M NaOH

Answer a available at the end of this section.

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The Common Ion Effect: Weak Bases Combined with Conjugate Acids

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

$$B(aq) + H_2O(l) \leftrightharpoons BH^+(aq) + OH^-(aq) \tag{17.2.3}$$

If the equilibrium constant for the reaction as written in Equation 17.2.3 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \dfrac{1}{K_b} = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 17.2.3 to shift to the left, consuming the added OH^-. As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier's principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.00, the pK_a of its conjugate acid is

$$pK_a = pK_w - pK_b = 14.0–5.0 = 9.0.$$

Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

$$BH^+(aq) + H_2O(l) \leftrightharpoons B(aq) + H_3O^+(aq) \tag{17.2.4}$$

Again, the equilibrium constant for the reverse of this reaction is very large: $K = 1/K_a = 10^9$. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 17.2.4 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the pH range over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 17.2.1, when $NaOH$ is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

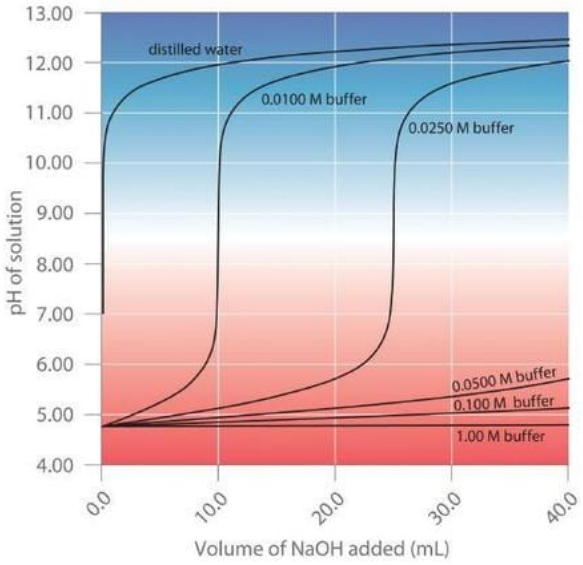


Figure 17.2.1: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)
Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M $NaOH$ to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of $NaOH$ solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the $NaOH$ solution results in only a relatively small change in pH.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 17.2.1 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \leftrightharpoons H^+ + A^-$, for which the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{17.2.5}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{17.2.6}$$

Taking the logarithm of both sides and multiplying both sides by –1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \tag{17.2.7}$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{17.2.8}$$

Replacing the negative logarithms in Equation 17.2.8,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{17.2.9}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{17.2.10}$$

Equation 17.2.9 and Equation 17.2.10 are both forms of the Henderson-Hasselbalch approximation, named after the two early 20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch approximation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch approximation is easily interpreted without the need for calculations:

- $[base] = [acid]$: Under these conditions,

  $$\frac{[base]}{[acid]} = 1$$

  in Equation 17.2.10. Because $\log 1 = 0$,

  $$pH = pK_a$$

  regardless of the actual concentrations of the acid and base. Recall that this corresponds to the midpoint in the titration of a weak acid or a weak base.
- $[base]/[acid] = 10$: In Equation 17.2.10, because $\log 10 = 1$,

  $$pH = pK_a + 1.$$
- $[base]/[acid] = 100$: In Equation 17.2.10, because $\log 100 = 2$,

  $$pH = pK_a + 2.$$

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = pK_a − 1. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

> If [base] = [acid] for a buffer, then pH = pK_a. Changing this ratio by a factor of 10 either way changes the pH by ±1 unit.

Example 17.2.2

What is the pH of a solution that contains

a. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)
b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?
c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch approximation (Equations 17.2.9 or 17.2.10) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 17.2.9), the pH of a solution that contains both a weak acid and its conjugate base is

$$pH = pK_a + \log([A-]/[HA]).$$

A

Inserting the given values into the equation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.215}{0.135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and $pK_a + 1$, or 4.75.

B

This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch approximation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.0215}{0.0135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends only on the ratio of the concentrations of the conjugate base and the acid, not on the magnitude of the concentrations. Because the [A¯]/[HA] ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

C

In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Equation 17.2.10, the more general form of the Henderson-Hasselbalch approximation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and $[acid] = [HPy^+] = 0.234\ M$. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall from Equation 16.23 that the pK_b of a weak base and the pK_a of its conjugate acid are related:

$$pK_a + pK_b = pK_w.$$

Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch approximation,

$$\begin{aligned} pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \\ &= 5.23 + \log\left(\frac{0.119}{0.234}\right) \\ &= 5.23 - 0.294 \\ &= 4.94 \end{aligned}$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

Exercise 17.2.2

What is the pH of a solution that contains

a. 0.333 M benzoic acid and 0.252 M sodium benzoate?
b. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer a available at the end of this section.

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The Henderson-Hasselbalch approximation ((Equation 17.2.9) can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 17.2.3.

Example 17.2.3

The buffer solution in Example 17.2.2 contained 0.135 M $\mathrm{HCO_2H}$ and 0.215 M $\mathrm{HCO_2Na}$ and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?
b. What is the final pH if 5.00 mL of 1.00 M $NaOH$ are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A. Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example 17.2.1 . Then calculate the amount of acid or base added.
B. Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch approximation (Equation 17.2.10) to obtain the pH.

Solution:

The added HCl (a strong acid) or NaOH (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

A We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100\ \cancel{mL}\left(\frac{0.135\,mmol\ \mathrm{HCO_2H}}{\cancel{mL}}\right) = 13.5\,mmol\,\mathrm{HCO_2H}$$

$$100\ \cancel{mL}\left(\frac{0.215\,mmol\ \mathrm{HCO_2^-}}{\cancel{mL}}\right) = 21.5\,mmol\,{}_2\mathrm{HCO^-}$$

The millimoles of $\mathrm{H^+}$ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00\ \cancel{mL}\left(\frac{1.00\,mmol\ \mathrm{H^+}}{\cancel{mL}}\right) = 5\,mmol\,\mathrm{H^+}$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$\mathrm{HCO^{2-}\,(aq) + H^{+}\,(aq) \rightleftharpoons HCO_2H\,(aq)}$$

initial amounts, changes in amounts, and final amounts:

	$HCO^{2-}(aq)$	$H^{+}(aq)$	$HCO_2H(aq)$
Initial	21.5 mmol	5.00 mmol	13.5 mmol
Change	–5.00 mmol	–5.00 mmol	+5.00 mmol
Final	16.5 mmol	~0 mmol	18.5 mmol

The final amount of H^+ in solution is given as "~0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 17.2.1 or the Henderson–Hasselbach approximation. Because we have performed many equilibrium calculations in this chapter, we'll take the latter approach. The Henderson-Hasselbalch approximation requires the concentrations of HCO_2^- and HCO_2H, which can be calculated using the number of millimoles (n) of each and the total volume (VT). Substituting these values into the Henderson-Hasselbalch approximation (Equation 17.2.10):

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \end{aligned}$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right) \\ &= 3.75\ - 0.050 = 3.70 \end{aligned}$$

Once again, this result makes sense on two levels. First, the addition of HClhas decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the pK_a and pK_a – 1.

A The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^-. The number of millimoles of OH^- in 5.00 mL of 1.00 M $NaOH$ is as follows:

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.

$$\mathrm{HCO_2H\,(aq) + OH^{-}\,(aq) \rightleftharpoons HCO_2^{-}\,(aq) + H_2O\,(l)}$$

initial amounts, changes in amounts, and final amounts

	$HCO_2H(aq)$	OH^-	$HCO_2^-(aq)$
Initial	13.5 mmol	5.00 mmol	21.5 mmol
Change	–5.00 mmol	–5.00 mmol	+5.00 mmol
Final	8.5 mmol	~0 mmol	26.5 mmol

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right) \\ &= 3.75 + 0.494 = 4.24 \end{aligned}$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO_2^-/HCO_2H ratio between 1 and 10.

Exercise 17.2.3

The buffer solution from Example 17.2.2 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

a. What is the final pH if 12.0 mL of 1.5 M NaOH are added to 250 mL of this solution?
b. What is the final pH if 12.0 mL of 1.5 M HCl are added?

Answer a available at the end of this section.

Only the amounts (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch approximation, not their concentrations.

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A Video Discussing the Change in pH with the Addition of a Strong Acid to a Buffer: The Change in pH with the Addition of a Strong Acid to a Buffer(opens in new window) [youtu.be]

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The Change in pH with the Addition of a Strong Base to a Buffer:

The Change in pH with the Addition of a Strong Base to a Buffer (opens in new window) [youtu.be]

The results obtained in Example 17.2.3 and its corresponding exercise demonstrate how little the pH of a well-chosen buffer

solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or $NaOH$ solution to 100 mL of an unbuffered solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M $NaOH$ would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

The most effective buffers contain **equal** concentrations of an acid and its conjugate base.

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure 17.2.2 for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to CH_3CO_2H from 1:1 reduces the buffer capacity of the solution.

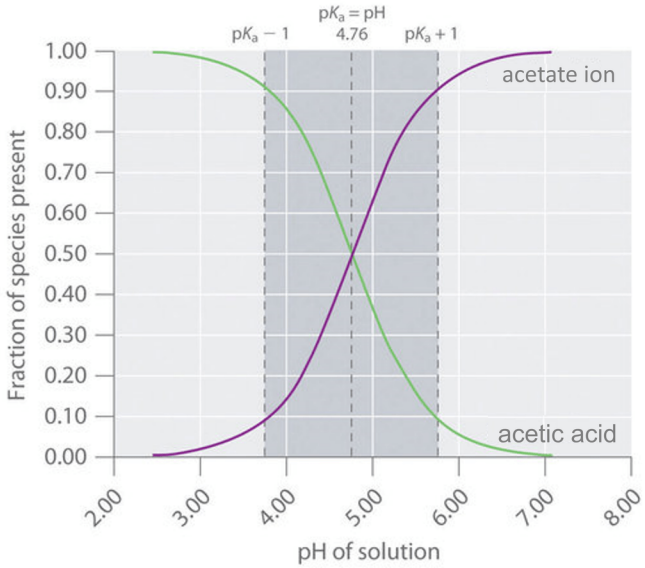


Figure 17.2.2: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $pH = pK_a \pm 1$). (CC BY-SA-NC; Anonymous by request)

Graph of mole fraction against pH of solution. The green line is acetic acid and the purple line is the acetate ion.

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The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5. Consider the schematic titration curve of a weak acid with a strong base shown in Figure 17.2.3. As indicated by the labels, the

region around pK_a corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat portion of the curve extends only from approximately a pH value of 1 unit less than the pK_a to approximately a pH value of 1 unit greater than the pK_a, which is why buffer solutions usually have a pH that is within ±1 pH units of the pK_a of the acid component of the buffer.

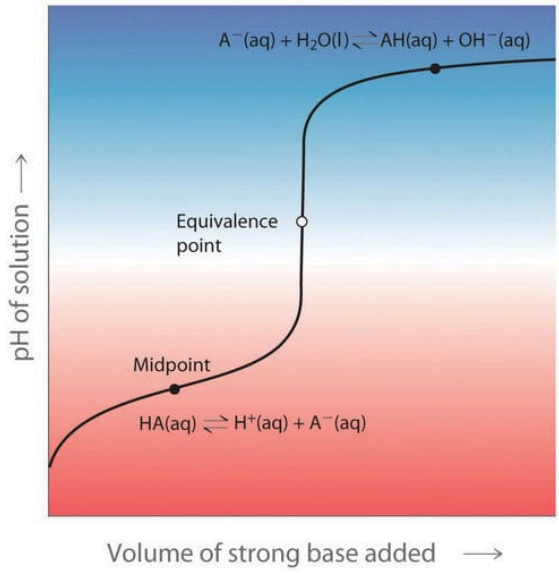


Figure 17.2.3: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)
Titration curves graph pH of solution against volume of strong base added. On the curve we look for the midpoints and equivalence points.

This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

In the region of the titration curve at the lower left, before the midpoint, the acid–base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to K_a. In the region of the titration curve at the upper right, after the midpoint, the acid–base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the weak acid with water, corresponding to K_b. However, we can calculate either K_a or K_b from the other because they are related by K_w.

Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

The acid–base equilibrium in the CO_2/HCO_3^- buffer system is usually written as follows:

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{17.2.11}$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 17.2.11 is a grossly oversimplified version of the CO_2/HCO_3^- system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3. Thus Equation 17.2.11 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C.

As shown in Equation 17.2.12, CO_2 is in equilibrium with H_2CO_3, but the equilibrium lies far to the left, with an H_2CO_3/CO_2 ratio less than 0.01 under most conditions:

$$\mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)} \tag{17.2.12}$$

with $K' = 4.0 \times 10^{-3}$ at 37°C. The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4}, which makes it a much stronger acid than Equation 17.2.11 suggests. Adding Equation 17.2.11 and Equation 17.2.12 and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

$$\mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)} \tag{17.2.13}$$

with $K' = 4.0 \times 10^{-3} (37\ ^\circ C)$

$$\mathrm{H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)} \tag{17.2.14}$$

with $K_a = 2.0 \times 10^{-4} (37\ ^\circ C)$

$$\mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)} \tag{17.2.15}$$

with $K = 8.0 \times 10^{-7} (37\ ^\circ C)$

The K value for the reaction in Equation 17.2.15 is the product of the true ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $CO_2\,(aq)$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

$$K = \frac{[\mathrm{H^+}][\mathrm{HCO_3^-}]}{[\mathrm{CO_2}]} = 8.0 \times 10^{-7} \tag{17.2.16}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to **Henry's law**,

$$[\mathrm{CO_2}] = kP_{\mathrm{CO_2}}$$

where k is the Henry's law constant for CO_2, which is $3.0 \times 10^{-5}\ \ M/mmHg$ at 37°C. Substituting this expression for $[CO_2]$ in Equation 17.2.16,

$$K = \frac{[\mathrm{H^+}][\mathrm{HCO_3^-}]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{\mathrm{CO_2}})}$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[\mathrm{HCO_3^-}]}{(3.0 \times 10^{-5} M/mm\ Hg)\ (P_{\mathrm{CO_2}})}\right) \tag{17.2.17}$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 17.2.4 plots the relationship between pH and $[HCO_3^-]$ under physiological conditions for several different values of P_{CO_2}, with normal pH and $[HCO_3^-]$ values indicated by the dashed lines.

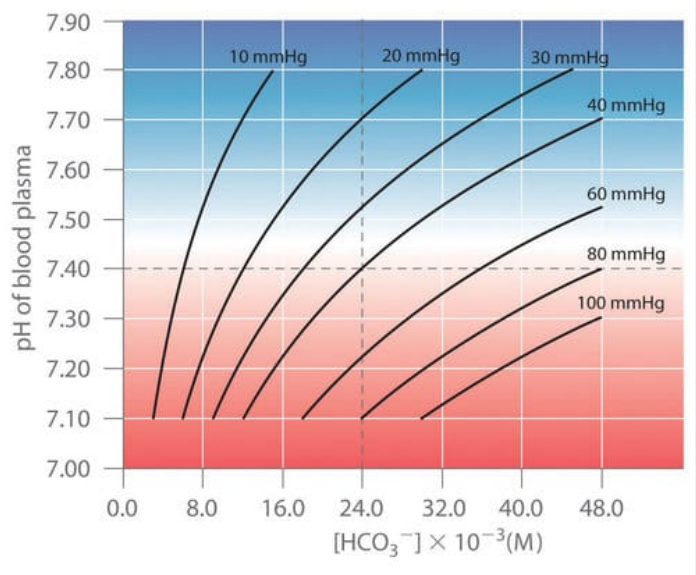


Figure 17.2.4: Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of P_{CO_2}. Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines. (CC BY-SA-NC; Anonymous by request)

According to Equation 17.2.17, adding a strong acid to the CO_2/HCO_3^- system causes $[HCO_3^-]$ to decrease as HCO_3^- is converted to CO_2. Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in P_{CO_2}. Because the change in $[HCO_3^-]/P_{CO_2}$ is small, Equation 17.2.17 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO_2 to form HCO_3^-, but CO_2 is replenished by the body, again limiting the change in both $[HCO_3^-]/P_{CO_2}$ and pH. The CO_2/HCO_3^- buffer system is an example of an open system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower P_{CO_2} at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[HCO_3^-]$. The increase in pH and decrease in $[HCO_3^-]$ in response to the decrease in P_{CO_2} are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.

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A Video Summary of the pH Curve for a Strong Acid/Strong Base Titration:

Summary of the pH Curve for a Strong Acid/Strong Base Titration(opens in new window) [youtu.be]

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the common ion effect. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its buffer capacity

depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the Henderson-Hasselbalch approximation, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

Answers

Exercise 17.2.1

11.16

1.3%

Exercise 17.2.2

4.08

9.68

Exercise 17.2.3

5.30

4.42

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17.3: Acid-Base Titrations

Learning Objectives

- To calculate the pH at any point in an acid–base titration.

In an acid–base titration, a buret is used to deliver measured volumes of an acid or a base solution of known concentration (the titrant) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the unknown). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a titration curve. The shape of the curve provides important information about what is occurring in solution during the titration.

Titrations of Strong Acids and Bases

Figure $17.3.1a$ shows a plot of the pH as 0.20 M HCl is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as HCl is added. Eventually the pH becomes constant at 0.70—a point well beyond its value of 1.00 with the addition of 50.0 mL of HCl (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M NaOH is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of NaOH as shown in Figure $17.3.1b$. As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.

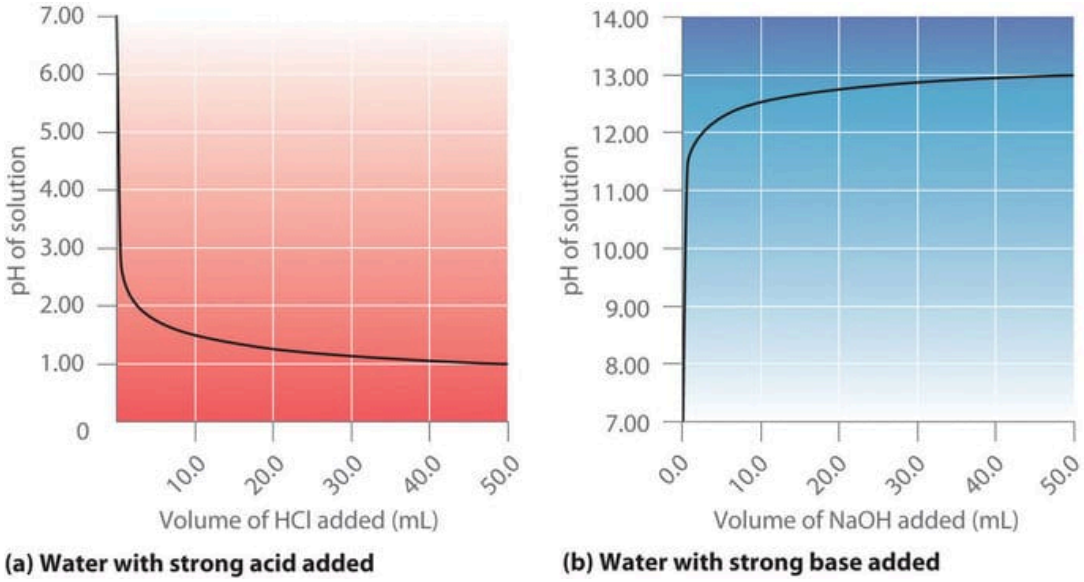


Figure $17.3.1$: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M $NaOH$. (CC BY-SA-NC; Anonymous by request)

The graphs of water with strong acid added and water with strong base added are inverses of each other.

Suppose that we now add 0.20 M NaOH to 50.0 mL of a 0.10 M solution of HCl. Because HCl is a strong acid that is completely ionized in water, the initial $[H^+]$ is 0.10 M, and the initial pH is 1.00. Adding NaOH decreases the concentration of H+ because of the neutralization reaction (Figure $17.3.2a$):

$$\mathrm{OH^- + H^+ \rightleftharpoons H_2O}.$$

Thus the pH of the solution increases gradually. Near the equivalence point, however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution, the pH increases much more rapidly because most of the H^+ ions originally present have been consumed. For the titration of a monoprotic strong acid (HCl) with a monobasic strong base ($NaOH$), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

$$moles\ of\ base = (volume)_b(molarity)_b V_b M_b = moles\ of\ acid = (volume)_a(molarity)_a = V_a M_a \tag{17.3.1}$$

If 0.20 M $NaOH$ is added to 50.0 mL of a 0.10 M solution of HCl, we solve for V_b:

$$V_b(0.20Me) = 0.025L = 25mL$$

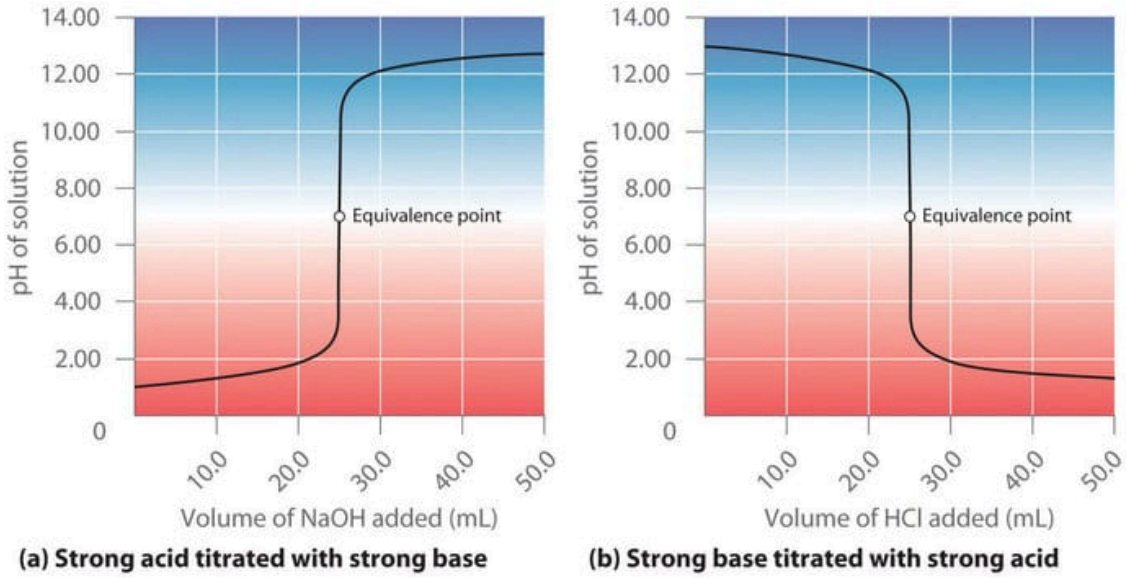


Figure 17.3.2: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M $NaOH$ is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M HCl is slowly added to 50.0 mL of 0.10 M $NaOH$, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more. (CC BY-SA-NC; Anonymous by request)

The titration curves of strong acid titrated with strong base and strong base titrated with strong acid are inverses of each other.

At the equivalence point (when 25.0 mL of $NaOH$ solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more $NaOH$ produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M $NaOH$.

As shown in Figure 17.3.2*b*, the titration of 50.0 mL of a 0.10 M solution of $NaOH$ with 0.20 M HCl produces a titration curve that is nearly the mirror image of the titration curve in Figure 17.3.2*a*. The pH is initially 13.00, and it slowly decreases as HCl is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M HCl.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on only the concentrations of the acid and base, not their identities.

> The shape of the titration curve involving a strong acid and a strong base depends only on their concentrations, not their identities.

Example 17.3.1: Hydrochloric Acid

Calculate the pH of the solution after 24.90 mL of 0.200 M $NaOH$ has been added to 50.00 mL of 0.100 M HCl.

Given: volumes and concentrations of strong base and acid

Asked for: pH

Strategy:

A. Calculate the number of millimoles of $\mathrm{H^+}$ and $\mathrm{OH^-}$ to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.
B. Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

Solution

A Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of $\mathrm{H^+}$ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$50.00 \cancel{mL}\left(\frac{0.100\ mmol\ HCl}{\cancel{mL}}\right) = 5.00\ mmol\ HCl = 5.00\ mmol\ H^+$$

The number of millimoles of NaOH added is as follows:

$$24.90 \cancel{mL}\left(\frac{0.200\ mmol\ NaOH}{\cancel{mL}}\right) = 4.98\ mmol\ NaOH = 4.98\ mmol\ OH^-$$

Thus $\mathrm{H^+}$ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of $\mathrm{OH^-}$ to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess $\mathrm{H^+}$ is 5.00 mmol – 4.98 mmol = 0.02 mmol of H^+.

B The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of $\mathrm{H^+}$ is as follows:

$$[H^+] = \frac{0.02\ mmol\ H^+}{74.90\ mL} = 3 \times 10^{-4}\ M$$

Hence,

$$pH \approx -\log[\mathrm{H^+}] = -\log(3 \times 10^{-4}) = 3.5$$

This is significantly less than the pH of 7.00 for a neutral solution.

Exercise 17.3.1

Calculate the pH of a solution prepared by adding $40.00\ \ mL$ of $0.237\ \ M\ HCl$ to $75.00\ \ mL$ of a $0.133M$ solution of $NaOH$.

Answer available at the end of this section.

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pH after the addition of 10 ml of Strong Base to a Strong Acid:

https://youtu.be/_cM1_-kdJ20 (opens in new window)

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pH at the Equivalence Point in a Strong Acid/Strong Base Titration:

https://youtu.be/7POGDA5Ql2M

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned previously, $[\mathrm{H^+}]$ of a solution of a weak acid (HA) is not equal to the concentration of the acid but depends on both its pK_a and its concentration. Because only a fraction of a weak acid dissociates, $[\backslash(\mathrm{H^+}]$ is less than $[\mathrm{HA}]$. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration.

Figure $17.3.3a$ shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M HCl shown in part (a) in Figure $17.3.2$. Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the HCl solution, and the pH changes more rapidly during the first part of the titration. Note also that the pH of the acetic acid solution at the equivalence point is greater than 7.00. That is, at the equivalence point, the solution is basic. In addition, the change in pH around the equivalence point is only about half as large as for the HCl titration; the magnitude of the pH change at the equivalence point depends on the pK_a of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess NaOH present, regardless of whether the acid is weak or strong.

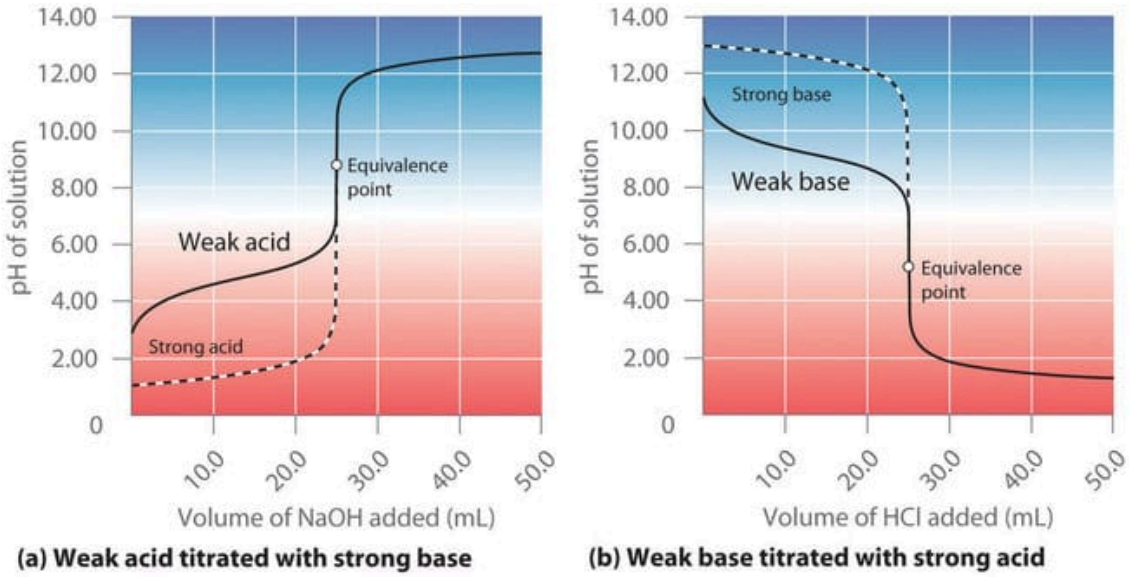


Figure 17.3.3: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH is shown as a dashed line. (b) As 0.200 M HCl is slowly added to 50.0 mL of 0.100 M NH3, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M NaOH with 0.200 M HCl is shown as a dashed line. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acid titrated with strong base and weak base titrated with strong acid are inverse of each other. These curves are shorter than the titration curves with strong acid and strong base.

> The shape of the titration curve of a weak acid or weak base depends heavily on their identities and the K_a or K_b.

The titration curve in Figure $17.3.3a$ was created by calculating the starting pH of the acetic acid solution before any NaOH is added and then calculating the pH of the solution after adding increasing volumes of $NaOH$. The procedure is illustrated in the following subsection and Example $17.3.2$ for three points on the titration curve, using the pK_a of acetic acid (4.76 at 25°C; $K_a = 1.7 \times 10^{-5}$.

Calculating the pH of a Solution of a Weak Acid or a Weak Base

As explained discussed, if we know K_a or K_b and the initial concentration of a weak acid or a weak base, we can calculate the pH of a solution of a weak acid or a weak base by setting up a ICE table (i.e, initial concentrations, changes in concentrations, and final concentrations). In this situation, the initial concentration of acetic acid is 0.100 M. If we define x as $[\mathrm{H}^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$\mathrm{CH_3CO_2H\,(aq) \rightleftharpoons H^+\,(aq) + CH_3CO_2{}^-}$$

table of concentrations for the ionization of 0.100 M acetic acid

ICE	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	0.100	1.00×10^{-7}	0
change	–x	+x	+x
final	0.100 – x	x	x

In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.45 and Equation 16.46 to check that this assumption is justified.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$
$$= \frac{(x)(x)}{0.100 - x}$$
$$\approx \frac{x^2}{0.100}$$
$$\approx 1.74 \times 10^{-5}$$

Solving this equation gives $x = [H^+] = 1.32 \times 10^{-3}\ M$. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$

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pH at the Start of a Weak Acid/Strong Base Titration: https://youtu.be/AtdBKfrfJNg

Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we add 5.00 mL of 0.200 M NaOH to 50.00 mL of 0.100 M CH_3CO_2H (part (a) in Figure 17.3.3). Because the neutralization reaction proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{17.3.2}$$

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the amounts of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation to determine $[\mathrm{H}^+]$ of the resulting solution.

Step 1

To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of $\mathrm{CH_3CO_2H}$ in the original solution and the amount of OH^- in the NaOH solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL}\ (0.100\ mmol(\mathrm{CH_3CO_2H})/\cancel{mL}) = 5.00\ mmol(\mathrm{CH_3CO_2H})$$

The NaOH solution contained

5.00 mL=1.00 mmol $NaOH$

Comparing the amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:

5.00 mmol CH_3CO_2H – 1.00 mmol OH^- = 4.00 mmol CH_3CO_2H

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following ICE table, which shows the numbers of moles of the various

species, not their concentrations.

$$\mathrm{CH_3CO_2H\,(aq) + OH^-\,(aq) \rightleftharpoons CH_3CO_2{}^-\,(aq) + H_2O\,(l)}$$

ICE table

ICE	$[\mathrm{CH_3CO_2H}]$	$[\mathrm{OH^-}]$	$[\mathrm{CH_3CO_2{}^-}]$
initial	5.00 mmol	1.00 mmol	0 mmol
change	–1.00 mmol	–1.00 mmol	+1.00 mmol
final	4.00 mmol	0 mmol	1.00 mmol

This ICE table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^-, but the amount of OH^- due to the autoionization of water is insignificant compared to the amount of OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2

To calculate $[\mathrm{H^+}]$ at equilibrium following the addition of $NaOH$, we must first calculate $[\mathrm{CH_3CO_2H}]$ and $[\mathrm{CH_3CO_2{}^-}]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M$$

$$[CH_3CO_2^-] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can calculate $[H^+]$ at equilibrium:

$$K_a = \frac{[CH_3CO_2^-]\,[H^+]}{[CH_3CO_2H]}$$

$$[H^+] = \frac{K_a\,[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{\left(1.72 \times 10^{-5}\right)\left(7.27 \times 10^{-2}\ M\right)}{\left(1.82 \times 10^{-2}\right)} = 6.95 \times 10^{-5}\ M$$

Calculating $-\log[\mathrm{H^+}]$ gives

$$pH = -\log(6.95 \times 10^{-5}) = 4.158.$$

Comparing the titration curves for HCl and acetic acid in Figure $17.3.3a$, we see that adding the same amount (5.00 mL) of 0.200 M NaOH to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for HCl (from 1.00 to 1.14) than for acetic acid (2.88 to 4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. In Example $17.3.2$, we calculate another point for constructing the titration curve of acetic acid.

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pH Before the Equivalence Point of a Weak Acid/Strong Base Titration:

https://youtu.be/znpwGCsefXc

Example 17.3.2

What is the pH of the solution after 25.00 mL of 0.200 M NaOH is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of OH^- and CH_3CO_2H. Determine which species, if either, is present in excess.
B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.
C. If excess acetate is present after the reaction with OH^-, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.
D. Calculate K_b using the relationship $K_w = K_aK_b$. Calculate [OH–] and use this to calculate the pH of the solution.

Solution

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

The initial numbers of millimoles of OH^- and CH_3CO_2H are as follows:

$$25.00 \text{ mL}(0.200 \text{ mmol OH–mL}=5.00 \text{ mmol } OH-$$

$$50.00\ mL(0.100 CH_3CO_2HL = 5.00 mmol\ CH_3CO_2H$$

The number of millimoles of OH^- equals the number of millimoles of CH_3CO_2H, so neither species is present in excess.

B Because the number of millimoles of OH^- added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)$$

results of the neutralization reaction

ICE	$[\mathrm{CH_3CO_2H}]$	$[\mathrm{OH^-}]$	$[\mathrm{CH_3CO_2^-}]$
initial	5.00 mmol	5.00 mmol	0 mmol
change	–5.00 mmol	–5.00 mmol	+5.00 mmol
final	0 mmol	0 mmol	5.00 mmol

C Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base with water to calculate [H+] at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

$$[\mathrm{CH_3CO_2}] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00 + 25.00)\ mL} = 6.67 \times 10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

$$\mathrm{CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)}$$

The equilibrium constant for this reaction is

$$K_b = \frac{K_w}{K_a} \tag{17.3.3}$$

where K_a is the acid ionization constant of acetic acid. We therefore define x as $[\mathrm{OH^-}]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$$H_2O_{(l)} + CH_3CO_{2(aq)}^- \rightleftharpoons CH_3CO_2H_{(aq)} + OH_{(aq)}^-$$

completed table of concentrations

	$[\mathrm{CH_3CO_2^-}]$	$[\mathrm{CH_3CO_2H}]$	$[\mathrm{OH^-}]$
initial	0.0667	0	1.00 × 10−7
change	−x	+x	+x
final	(0.0667 − x)	x	x

D We can obtain K_b by substituting the known values into Equation 17.3.3:

$$K_b = \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.80 \times 10^{-10} \tag{17.3.4}$$

Substituting the expressions for the final values from the ICE table into Equation 17.3.4 and solving for x:

$$\frac{x^2}{0.0667} = 5.80 \times 10^{-10}$$

$$x = \sqrt{(5.80 \times 10^{-10})(0.0667)}$$

$$= 6.22 \times 10^{-6}$$

Thus $[OH^-] = 6.22 \times 10^{-6}\ M$ and the pH of the final solution is 8.794 (Figure 17.3.3a). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce $\mathrm{OH^-}$.

Exercise 17.3.2

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The pK_b of ammonia is 4.75 at 25°C.

Answer available at the end of this section.

As shown in part (b) in Figure 17.3.3, the titration curve for NH3, a weak base, is the reverse of the titration curve for acetic acid. In particular, the pH at the equivalence point in the titration of a weak base is less than 7.00 because the titration produces an acid.

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure $17.3.4$ illustrates the shape of titration curves as a function of the pK_a or the pK_b. As the acid or the base being titrated becomes weaker (its pK_a or pK_b becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.

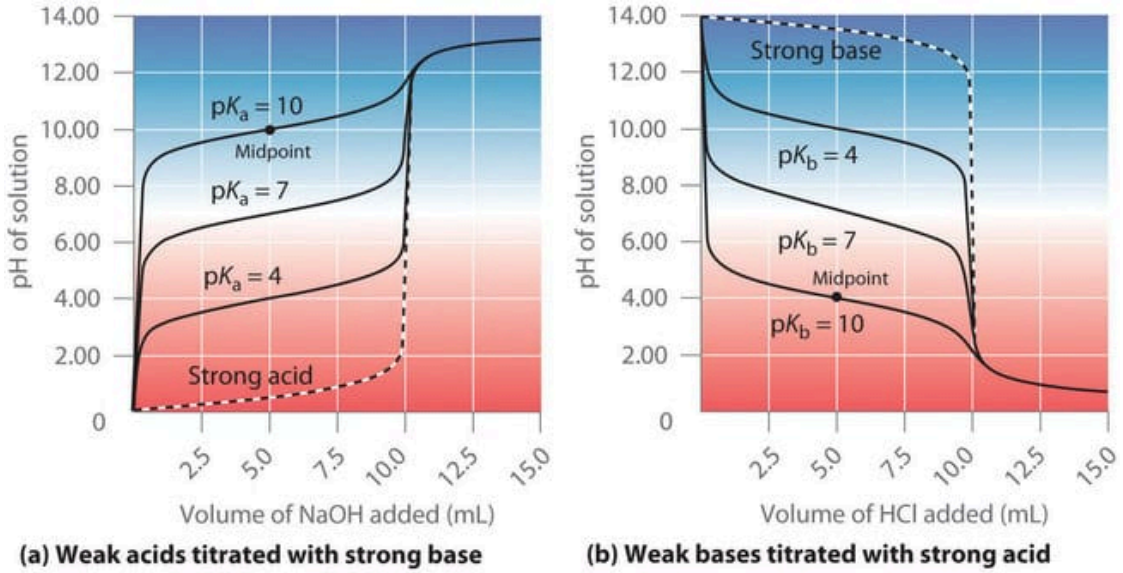


Figure $17.3.4$: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added to 10.00 mL of 1.00 M solutions of weak acids with the indicated pK_a values. (b) Solution pH as a function of the volume of 1.00 M HCl added to 10.00 mL of 1.00 M solutions of weak bases with the indicated pK_b values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to pK_a = 10 and pK_b = 10. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acids with strong base and weak bases titrated with strong acid are inverses of each other. Three weak acids and three weak bases with pKa and pKb of 4, 7, and 10 are used.

One point in the titration of a weak acid or a weak base is particularly important: the midpoint of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in Figures $17.3.4a$ and $17.3.4b$ for the two shallowest curves. By definition, at the midpoint of the titration of an acid, [HA] = [A–]. Recall that the ionization constant for a weak acid is as follows:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

If $[HA] = [A^-]$, this reduces to $K_a = [H_3O^+]$. Taking the negative logarithm of both sides,

$$-\log K_a = -\log[H_3O+]$$

From the definitions of pK_a and pH, we see that this is identical to

$$pK_a = pH \tag{17.3.5}$$

Thus the pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid, as indicated in part (a) in Figure $17.3.4$ for the weakest acid where we see that the midpoint for pK_a = 10 occurs at pH = 10. Titration methods can therefore be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base).

> The pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid.

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group

is titrated first, followed by the next most acidic, and so forth. If the pK_a values are separated by at least three pK_a units, then the overall titration curve shows well-resolved "steps" corresponding to the titration of each proton. A titration of the triprotic acid H_3PO_4 with NaOH is illustrated in Figure $17.3.5$ and shows two well-defined steps: the first midpoint corresponds to pK_a1, and the second midpoint corresponds to pK_a2. Because HPO_4^{2-} is such a weak acid, pK_a3 has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

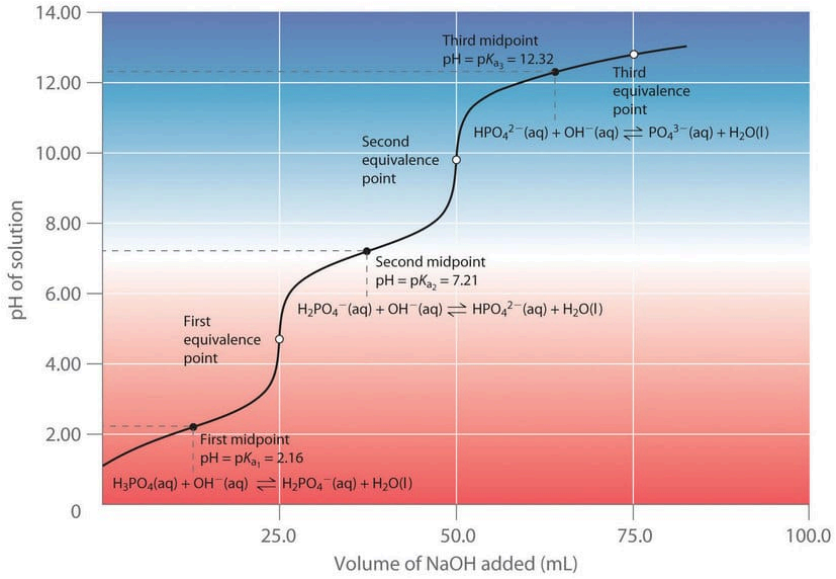
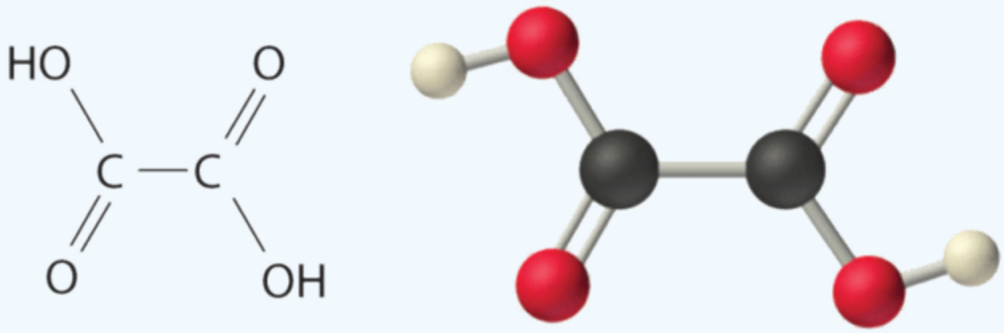


Figure $17.3.5$: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^{2-}$ at pH ≈ 9.8. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined. (CC BY-SA-NC; Anonymous by request)

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure $17.3.5$. The initial pH is high, but as acid is added, the pH decreases in steps if the successive pK_b values are well separated. Table E1 lists the ionization constants and pK_a values for some common polyprotic acids and bases.

Example 17.3.3

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M NaOH solution to 100.0 mL of a 0.0510 M solution of oxalic acid ($\mathrm{HO_2CCO_2H}$), a diprotic acid (abbreviated as $\mathrm{H_2ox}$). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($\mathrm{O_2CCO_2^{2-}}$, abbreviated $\mathrm{ox^{2-}}$).Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as $\mathrm{Ca^{2+}}$ are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



oxalic acid

Given: volume and concentration of acid and base

Asked for: pH

Strategy:

A. Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.
B. Calculate the concentrations of all the species in the final solution. Determine $[H+]$ and convert this value to pH.

Solution:

A Table E5 gives the pK_a values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

$$100.00\,\cancel{mL}\left(\frac{0.510\ mmol\ H_2ox}{\cancel{mL}}\right) = 5.10\ mmol\ H_2ox$$

$$55.00\,\cancel{mL}\left(\frac{0.120\ mmol\ NaOH}{\cancel{mL}}\right) = 6.60\ mmol\ NaOH$$

The strongest acid (H_2ox) reacts with the base first. This leaves (6.60 – 5.10) = 1.50 mmol of OH^- to react with Hox–, forming ox^{2-} and H_2O. The reactions can be written as follows:

$$\underset{5.10\ mmol}{H_2ox} + \underset{6.60\ mmol}{OH^-} \rightarrow \underset{5.10\ mmol}{Hox^-} + \underset{5.10\ mmol}{H_2O}$$

$$\underset{5.10\ mmol}{Hox^-} + \underset{1.50\ mmol}{OH^-} \rightarrow \underset{1.50\ mmol}{ox^{2-}} + \underset{1.50\ mmol}{H_2O}$$

In tabular form,

Solutions to Example 17.3.3

	H_2ox	OH^-	Hox^-	ox^{2-}
initial	5.10 mmol	6.60 mmol	0 mmol	0 mmol
change (step 1)	–5.10 mmol	–5.10 mmol	+5.10 mmol	0 mmol
final (step 1)	0 mmol	1.50 mmol	5.10 mmol	0 mmol
change (step 2)	—	–1.50 mmol	–1.50 mmol	+1.50 mmol
final	0 mmol	0 mmol	3.60 mmol	1.50 mmol

B The equilibrium between the weak acid (Hox^-) and its conjugate base (ox^{2-}) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}$. To calculate the pH of the solution, we need to know $[\mathrm{H}^+]$, which is determined using exactly the same method as in the acetic acid titration in Example 17.3.2:

$$\text{final volume of solution} = 100.0\,mL + 55.0\,mL = 155.0\,mL$$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$[Hox^-] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$[ox^{2-}] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2} = \frac{[ox^{2-}]\,[H^+]}{[Hox^-]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$[H^+] = \frac{K_{a2}\,[Hox^-]}{[ox^{2-}]} = \frac{\left(1.6 \times 10^{-4}\right)\left(2.32 \times 10^{-2}\right)}{\left(9.68 \times 10^{-3}\right)} = 3.7 \times 10^{-4}\ M$$

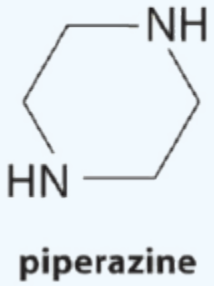
So

$$pH = -\log\left[H^+\right] = -\log\left(3.7 \times 10^{-4}\right) = 3.43$$

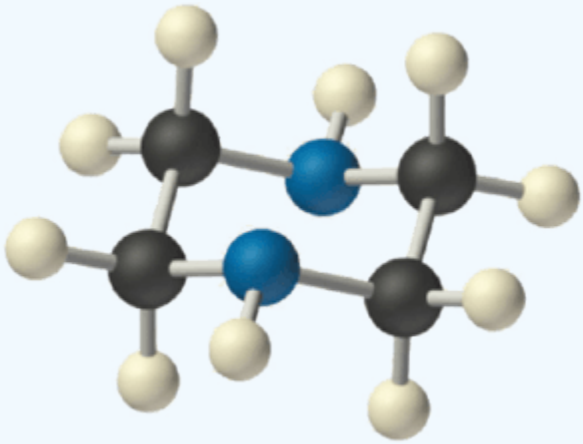
This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}), but we added only enough to titrate less than half of the second, less acidic proton, with pK_{a2}. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to pK_{a2}.

Exercise 17.3.3: Piperazine

Piperazine is a diprotic base used to control intestinal parasites (“worms”) in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (pK_{b1} = 4.27, pK_{b2} = 8.67). If the dog’s stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



piperazine



Answer available at the end of this section.

Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated (phenolphthalein, for example), which makes them particularly useful.

We can describe the chemistry of indicators by the following general equation:

$$\mathrm{HIn\,(aq)} \rightleftharpoons \mathrm{H^+\,(aq)} + \mathrm{In^-\,(aq)}$$

where the protonated form is designated by HIn and the conjugate base by $\mathrm{In^-}$. The ionization constant for the deprotonation of indicator HIn is as follows:

$$K_{In} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \tag{17.3.6}$$

The pK_{in} (its pK_a) determines the pH at which the indicator changes color.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH. Similarly, *Hydrangea macrophylla* flowers can be blue, red, pink, light purple, or dark purple depending on the soil pH (Figure $17.3.6$). Acidic soils will produce blue flowers, whereas alkaline soils will produce pinkish flowers.

Irrespective of the origins, a good indicator must have the following properties:

- The color change must be easily detected.
- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a pK_{in} that is within one pH unit of the expected pH at the equivalence point of the titration.



Figure $17.3.6$: Naturally occurring pH indicators can be found in red cabbage and Hydrangea macrophylla flowers. Red Cabbage image (CC BY-SA 3.0; KENPEI via Wikipedia) and Hydrangea macrophylla flowers (pixabay).

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure $17.3.7$ shows the approximate pH range over which some common indicators change color and their change in color. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change color twice at widely separated pH values.

Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

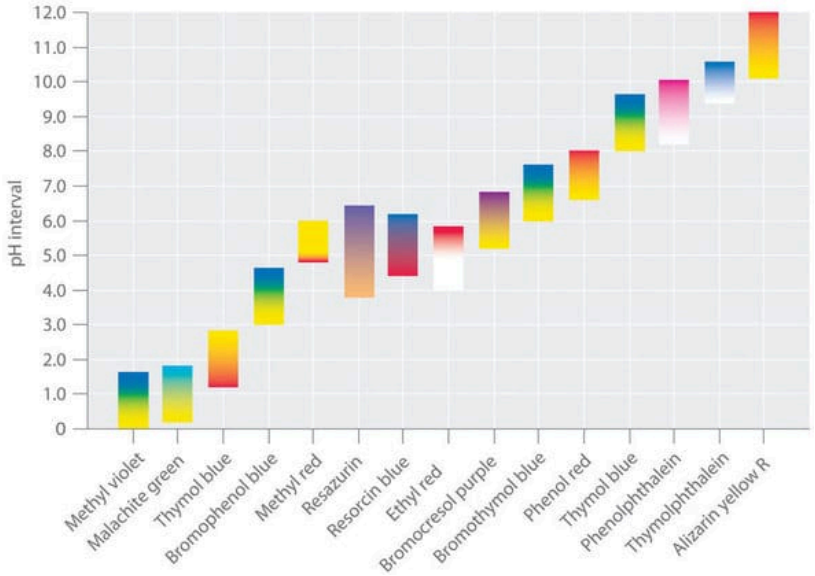


Figure 17.3.7: Some Common Acid–Base Indicators. Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

It is important to be aware that an indicator does not change color abruptly at a particular pH value; instead, it actually undergoes a pH titration just like any other acid or base. As the concentration of HIn decreases and the concentration of In– increases, the color of the solution slowly changes from the characteristic color of HIn to that of In–. As we will see later, the [In–]/[HIn] ratio changes from 0.1 at a pH one unit below pKin to 10 at a pH one unit above pKin. Thus most indicators change color over a pH range of about two pH units.

We have stated that a good indicator should have a pKin value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point. In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors, as illustrated in Figure 17.3.8. This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M $NaOH$. The pH ranges over which two common indicators (methyl red, $pK_{in} = 5.0$, and phenolphthalein, $pK_{in} = 9.5$) change color are also shown. The horizontal bars indicate the pH ranges over which both indicators change color cross the HCl titration curve, where it is almost vertical. Hence both indicators change color when essentially the same volume of NaOH has been added (about 50 mL), which corresponds to the equivalence point. In contrast, the titration of acetic acid will give very different results depending on whether methyl red or phenolphthalein is used as the indicator. Although the pH range over which phenolphthalein changes color is slightly greater than the pH at the equivalence point of the strong acid titration, the error will be negligible due to the slope of this portion of the titration curve. Just as with the HCl titration, the phenolphthalein indicator will turn pink when about 50 mL of NaOH has been added to the acetic acid solution. In contrast, methyl red begins to change from red to yellow around pH 5, which is near the midpoint of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of NaOH will therefore cause the methyl red indicator to change color, resulting in a huge error.

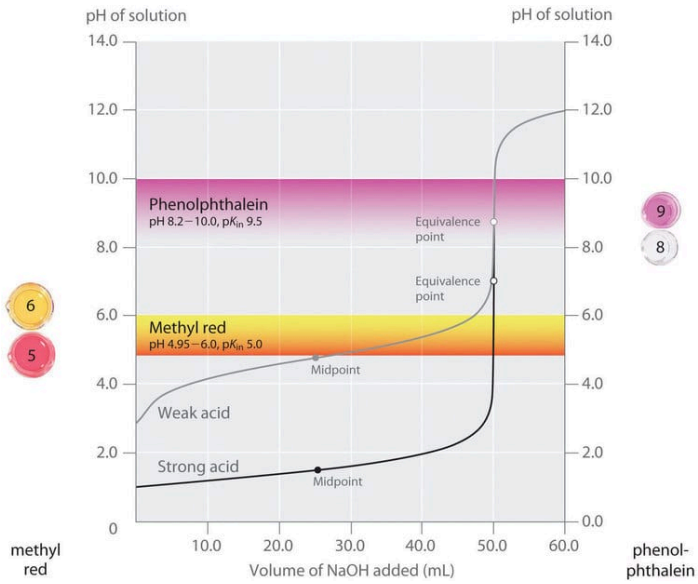


Figure 17.3.8: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

If the pH of the solution is between 4.95 and 6 then methyl red should be used. If the pH is between 8,2 and 10 then phenolphthalein should be used.

The graph shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M $NaOH$. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change color at the equivalence point for the titration of the strong acid. In contrast, the pKin for methyl red (5.0) is very close to the pK_a of acetic acid (4.76); the midpoint of the color change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a pKin between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with pKin > 7.0, should be used. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with pKin < 7.0, should be used.

The existence of many different indicators with different colors and pKin values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting color with the standards printed on the container (Figure 17.3.9).

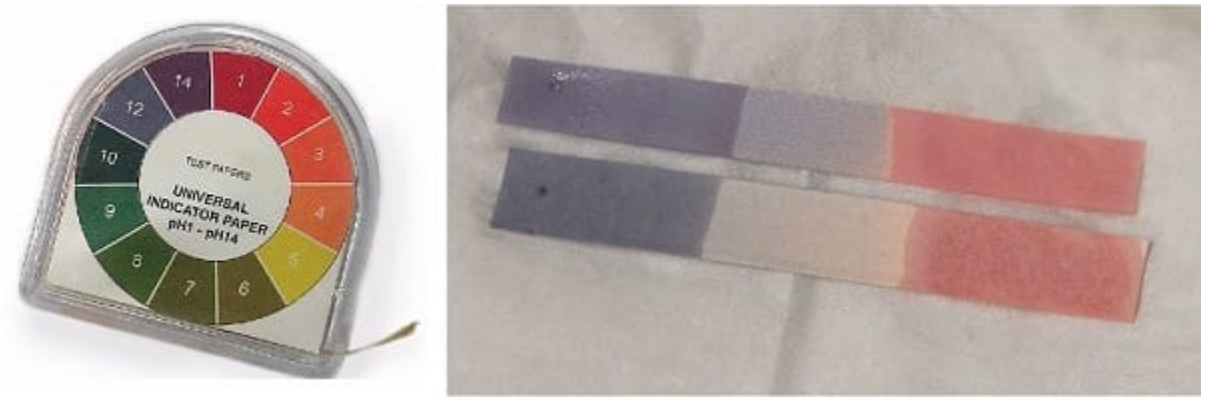


Figure 17.3.9: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)

YouTube Video

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pH Indicators: pH Indicators(opens in new window) [youtu.be]

Summary and Takeaway

Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the pK_a, and the pK_b of the system. The shape of a titration curve, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The equivalence point of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases, however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the midpoint, the point halfway on the titration curve to the equivalence point, is equal to the pK_a of the weak acid or the pK_b of the weak base. Thus titration methods can be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base). Acid–base indicators are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

Answers

Exercise 17.3.1

11.6

Exercise 17.3.2

9.23

Exercise 17.3.3**: Piperazine**

pH=4.9

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17.4: Solubility Equilibria

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{17.4.1}$$

As you will discover in Section 17.4 and in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\mathrm{Ca}^{2+}]^3[\mathrm{PO}_4^{3-}]^2}{[\mathrm{Ca}_3(\mathrm{PO}_4)_2]} \tag{17.4.2}$$

$$[\mathrm{Ca}_3(\mathrm{PO}_4)_2]K = K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}]^3[\mathrm{PO}_4^{3-}]^2 \tag{17.4.3}$$

At 25°C and pH 7.00, Ksp for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table 17.4.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 17.4.2 and 17.4.3, changes in pH can affect the solubility of a compound as discussed later.

As with any K, the concentration of a pure solid does not appear explicitly in K_{sp}.

Table 17.4.1: Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	K_{sp}		Solid	Color	K_{sp}
Acetates				**Iodides**		
$Ca(O_2CCH_3)_2{\cdot}3H_2O$	white	4×10^{-3}		Hg_2I_2*	yellow	5.2×10^{-29}
Bromides				PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}		**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}		$Ag_2C_2O_4$	white	5.40×10^{-12}
***These contain the Hg_2^{2+} ion.**						

Solid	Color	K_{sp}		Solid	Color	K_{sp}
Carbonates				$MgC_2O_4 \cdot 2H_2O$	white	4.83×10^{-6}
$CaCO_3$	white	3.36×10^{-9}		PbC_2O_4	white	4.8×10^{-10}
$PbCO_3$	white	7.40×10^{-14}		**Phosphates**		
Chlorides				Ag_3PO_4	white	8.89×10^{-17}
AgCl	white	1.77×10^{-10}		$Sr_3(PO_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2*	white	1.43×10^{-18}		$FePO_4 \cdot 2H_2O$	pink	9.91×10^{-16}
$PbCl_2$	white	1.70×10^{-5}		**Sulfates**		
Chromates				Ag_2SO_4	white	1.20×10^{-5}
$CaCrO_4$	yellow	7.1×10^{-4}		$BaSO_4$	white	1.08×10^{-10}
$PbCrO_4$	yellow	2.8×10^{-13}		$PbSO_4$	white	2.53×10^{-8}
Fluorides				**Sulfides**		
BaF_2	white	1.84×10^{-7}		Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}		CdS	yellow	8.0×10^{-27}
Hydroxides				PbS	black	8.0×10^{-28}
$Ca(OH)_2$	white	5.02×10^{-6}		ZnS	white	1.6×10^{-24}
$Cu(OH)_2$	pale blue	1×10^{-14}				
$Mn(OH)_2$	light pink	1.9×10^{-13}				
$Cr(OH)_3$	gray-green	6.3×10^{-31}				
$Fe(OH)_3$	rust red	2.79×10^{-39}				

***These contain the Hg_2^{2+} ion.**

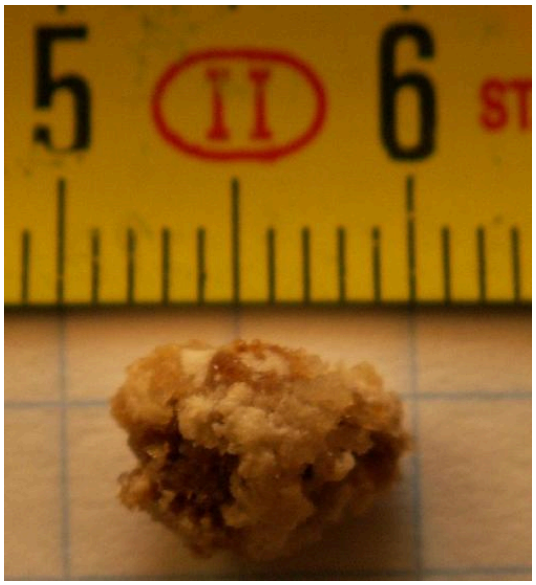
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Definition of a Solubility Product: Definition of a Solubility Product(opens in new window) [youtu.be]

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the molar concentrations of the component ions.



A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2)·H_2O$ and $Ca_3(PO_4)_2$. from Wikipedia.

Example 17.4.1

Calcium oxalate monohydrate [$Ca(O_2CCO_2)·H_2O$, also written as $CaC_2O_4·H_2O$] is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp}.

Given: solubility in g/100 mL

Asked for: K_{sp}

Strategy:

A. Write the balanced dissolution equilibrium and the corresponding solubility product expression.
B. Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp}.

Solution

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:

$$\mathrm{Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {^-O_2CCO_2^-}(aq) + H_2O(l)} \qquad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{ox^{2-}}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine $[Ca^{2+}]$ and $[ox^{2-}]$ at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36 \times 10^{-4}\ \text{g}}{146.1\ \text{g/mol}} = 5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2\cdot)\text{H}_2\text{O}}{100\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1.00\ \text{L}}\right) = 5.04 \times 10^{-5}\ \text{mol/L} = 5.04 \times 10^{-5}\ \text{M}$$

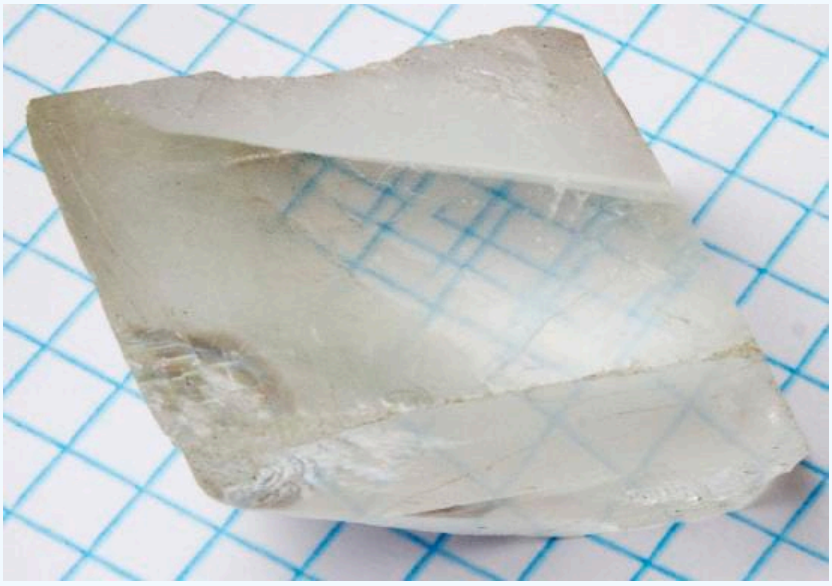
Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04×10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

Exercise 17.4.1: Calcite

One crystalline form of calcium carbonate ($CaCO_3$) is "calcite", found as both a mineral and a structural material in many organisms. Calcite is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. from Wikipedia

The solubility of calcite in water is 0.67 mg/100 mL. Calculate its K_{sp}.

Answer

4.5×10^{-9}

The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.

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Finding Ksp from Ion Concentrations: Finding Ksp from Ion Concentrations(opens in new window) [youtu.be]

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 17.4.1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations (ICE Tables), remembering that the concentration of the pure solid is essentially constant.

Example 17.4.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

a. the molarity of ions produced in solution
b. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A. Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.
B. Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

A. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 17.4.2) is shown in the following ICE table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Solutions to Example 17.4.2

	Ca3(PO4)2	[Ca2+]	$[PO_4^{3-}]$
initial	pure solid	0	0
change	—	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

Although the amount of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2 \quad (17.4.4)$$

$$2.07 \times 10^{-33} = 108x^5 \quad (17.4.5)$$

$$1.92 \times 10^{-35} = x^5 \quad (17.4.6)$$

$$1.14 \times 10^{-7}\ \text{M} = x \quad (17.4.7)$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is 2*x* and 3*x*, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

b. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g}\ Ca_3(PO_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g}\ Ca_3(PO_4)_2$$

Exercise 17.4.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

a. the molarity of a saturated solution
b. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer

a. 1.28×10^{-4} M
b. 3.54 mg

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Finding the Solubility of a Salt: Finding the Solubility of a Salt (opens in new window) [youtu.be]

The Ion Product

The **ion product (Q)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (Q) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations.

The ion product *Q* is analogous to the reaction quotient *Q* for gaseous equilibria.

As summarized in Figure 17.4.1, there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.

- $Q = K_{sp}$. The solution is saturated and at equilibrium.
- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

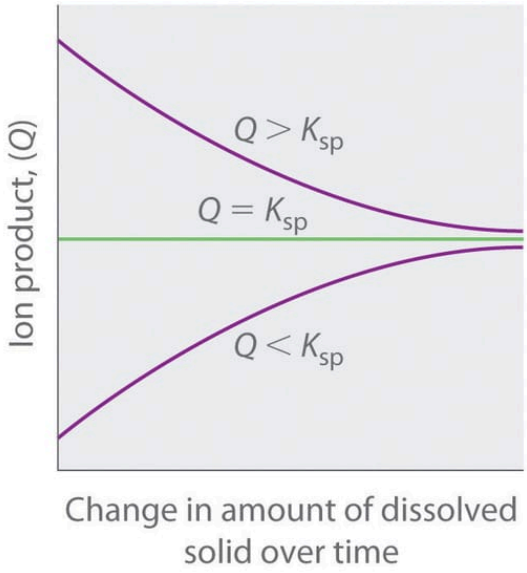


Figure 17.4.1: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium (Q = K_{sp}). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until Q = K_{sp}. If Q = K_{sp}, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

Graph of ion product against change in amount of dissolved solid over time. The purple curves are when Q is greater or less than Ksp. The green line is when Q is equal to Ksp.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 17.4.3

We mentioned that barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a "barium milkshake" is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

A. Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp}.
B. Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).
C. Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution

A The only slightly soluble salt that can be formed when these two solutions are mixed is $BaSO_4$ because NaCl is highly soluble. The equation for the precipitation of $BaSO_4$ is as follows:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The solubility product expression is as follows:

$$K_{sp} = [Ba^{2+}][SO_4{}^{2-}] = 1.08\times10^{-10}$$

B To solve this problem, we must first calculate the ion product—$Q = [Ba^{2+}][SO_4{}^{2-}]$—using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of $BaCl_2$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles } Ba^{2+} = 100 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{3.2\times10^{-4} \text{ mol}}{1 \text{ L}}\right) = 3.2\times10^{-5} \text{ mol } Ba^{2+}$$

$$[Ba^{2+}] = \left(\frac{3.2\times10^{-5} \text{ mol } Ba^{2+}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 2.9\times10^{-4} \text{ M } Ba^{2+}$$

Similarly, the concentration of $SO_4{}^{2-}$ after mixing is the total number of moles of $SO_4{}^{2-}$ in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles } SO_4^{2-} = 10.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.0020 \text{ mol}}{1 \text{ L}}\right) = 2.0\times10^{-5} \text{ mol } SO_4^{2-}$$

$$[SO_4^{2-}] = \left(\frac{2.0\times10^{-5} \text{ mol } SO_4^{2-}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 1.8\times10^{-4} \text{ M } SO_4^{2-}$$

We can now calculate Q:

$$Q = [Ba^{2+}][SO_4{}^{2-}] = (2.9\times10^{-4})(1.8\times10^{-4}) = 5.2\times10^{-8}$$

C We now compare Q with the K_{sp}. If $Q > K_{sp}$, then $BaSO_4$ will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when $[Ba^{2+}][SO_4{}^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

Exercise 17.4.3

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5}M solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer available at the end of this section.

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Determining if a Precipitate forms (The Ion Product): Determining if a Precipitate forms (The Ion Product)(opens in new window) [youtu.be]

The Common Ion Effect and Solubility

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. Adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion. The exceptions generally involve the formation of complex ions, which is discussed later.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains $3 \times (1.14 \times 10^{-7}\ M) = 3.42 \times 10^{-7}$ M Ca^{2+} and $2 \times (1.14 \times 10^{-7}\ M) = 2.28 \times 10^{-7}$ M PO_4^{3-}, according to the stoichiometry shown in Equation 17.4.1 (neglecting hydrolysis to form HPO_4^{2-} as described in Chapter 16). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 17.4.1 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

The common ion effect usually **decreases** the solubility of a sparingly soluble salt.

Example 17.4.4

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.
B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in [Ca^{2+}] is once again $+3x$, and the change in [PO_4^{3-}] is $+2x$. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)}$$

Solutions to Example 17.4.4

	Ca3(PO4)2	[Ca^{2+}]	[PO_4^{3-}]
initial	pure solid	0.20	0
change	—	$+3x$	$+2x$
final	pure solid	$0.20 + 3x$	$2x$

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07\times10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that $x << 0.20$. Thus $(0.20 + 3x)$ M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$\begin{aligned} K_{sp} = (0.20)^3(2x)^2 &= 2.07 \times 10^{-33} \\ x^2 &= 6.5 \times 10^{-32} \\ x &= 2.5 \times 10^{-16}\ \text{M} \end{aligned}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 17.4.2—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

Exercise 17.4.4

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer available at the end of this section.

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The Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products(opens in new window) [youtu.be]

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions. In contrast, the ion product (Q) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

Answers

Exercise 17.4.3

yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)

Exercise 17.4.4

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)

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17.5: Factors that Affect Solubility

Learning Objectives

- To understand the factors that determine the solubility of ionic compounds.

The solubility product of an ionic compound describes the concentrations of ions in equilibrium with a solid, but what happens if some of the cations become associated with anions rather than being completely surrounded by solvent? Then predictions of the total solubility of the compound based on the assumption that the solute exists solely as discrete ions would differ substantially from the actual solubility, as would predictions of ionic concentrations. In general, four situations explain why the solubility of a compound may be other than expected: ion pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH.

Ion-Pair Formation

An **ion pair** consists of a cation and an anion that are in intimate contact in solution, rather than separated by solvent (Figure 17.5.1). The ions in an ion pair are held together by the same attractive electrostatic force in ionic solids. As a result, the ions in an ion pair migrate as a single unit, whose net charge is the sum of the charges on the ions. In many ways, we can view an ion pair as a species intermediate between the ionic solid (in which each ion participates in many cation–anion interactions that hold the ions in a rigid array) and the completely dissociated ions in solution (where each is fully surrounded by water molecules and free to migrate independently).

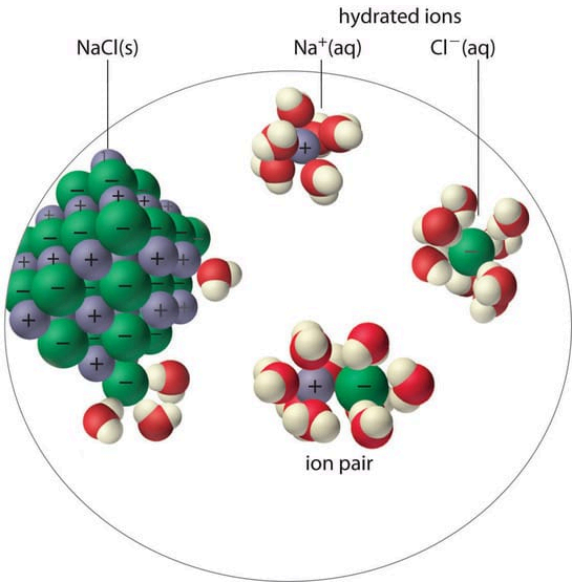


Figure 17.5.1: Ion-Pair Formation. In an ion pair, the cation and the anion are in intimate contact in solution and migrate as a single unit. They are not completely dissociated and individually surrounded by solvent molecules, as are the hydrated ions, which are free to migrate independently.

As illustrated for calcium sulfate in the following equation, a second equilibrium must be included to describe the solubility of salts that form ion pairs:

$$\mathrm{CaSO_4(s) \rightleftharpoons \underbrace{Ca^{2+} \cdot SO_4^{2-}(aq)}_{\text{ion pair}} \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)} \tag{17.5.1}$$

The ion pair is represented by the symbols of the individual ions separated by a dot, which indicates that they are associated in solution. The formation of an ion pair is a dynamic process, just like any other equilibrium, so a particular ion pair may exist only briefly before dissociating into the free ions, each of which may later associate briefly with other ions.

Ion-pair formation can have a major effect on the measured solubility of a salt. For example, the measured K_{sp} for calcium sulfate is 4.93×10^{-5} at 25°C. The solubility of $CaSO_4$ should be 7.02×10^{-3} M if the only equilibrium involved were as follows:

$$\mathrm{CaSO_4\,(s) \rightleftharpoons Ca^{2+}\,(aq) + SO_4^{2-}\,(aq)} \tag{17.5.2}$$

In fact, the experimentally measured solubility of calcium sulfate at 25°C is 1.6×10^{-2} M, almost twice the value predicted from its K_{sp}. The reason for the discrepancy is that the concentration of ion pairs in a saturated $\mathrm{CaSO_4}$ solution is almost as high as the concentration of the hydrated ions. Recall that the magnitude of attractive electrostatic interactions is greatest for small, highly charged ions. Hence ion pair formation is most important for salts that contain M^{2+} and M^{3+} ions, such as Ca^{2+} and La^{3+}, and is relatively unimportant for salts that contain monopositive cations, except for the smallest, Li^+. We therefore expect a saturated solution of $\mathrm{CaSO_4}$ to contain a high concentration of ion pairs and its solubility to be greater than predicted from its K_{sp}.

The formation of ion pairs increases the solubility of a salt.

Incomplete Dissociation

A molecular solute may also be more soluble than predicted by the measured concentrations of ions in solution due to incomplete dissociation. This is particularly common with weak organic acids. Although strong acids (HA) dissociate completely into their constituent ions (H^+ and A^-) in water, weak acids such as carboxylic acids do not ($K_a = 1.5 \times 10^{-5}$). However, the molecular (undissociated) form of a weak acid (HA) is often quite soluble in water; for example, acetic acid (CH_3CO_2H) is completely miscible with water. Many carboxylic acids, however, have only limited solubility in water, such as benzoic acid ($C_6H_5CO_2H$), with $K_a = 6.25 \times 10^{-5}$. Just as with calcium sulfate, we need to include an additional equilibrium to describe the solubility of benzoic acid:

$$\mathrm{C_6H_5CO_2H\,(s) \rightleftharpoons C_6H_5CO_2H\,(aq) \rightleftharpoons C_6H_5CO_2^-\,(aq) + H^+\,(aq)}$$

In a case like this, measuring only the concentration of the ions grossly underestimates the total concentration of the organic acid in solution. In the case of benzoic acid, for example, the pH of a saturated solution at 25°C is 2.85, corresponding to $[H^+] = [C_6H_5CO_2^-] = 1.4 \times 10^{-3}$ M. The total concentration of benzoic acid in the solution, however, is 2.8×10^{-2} M. Thus approximately 95% of the benzoic acid in solution is in the form of hydrated neutral molecules—$C_6H_5CO_2H_{(aq)}$—and only about 5% is present as the dissociated ions (Figure 17.5.2).

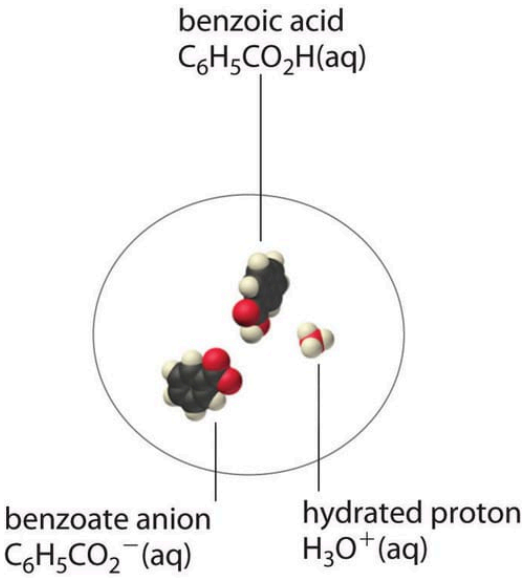


Figure 17.5.2: Incomplete Dissociation of a Molecular Solute. In a saturated solution of benzoic acid in water at 25°C, only about 5% of the dissolved benzoic acid molecules are dissociated to form benzoate anions and hydrated protons. The remaining 95% exists in solution in the form of hydrated neutral molecules. (H_2O molecules are omitted for clarity.)

Although ion pairs, such as $Ca^{2+}{\cdot}SO_4^{2-}$, and undissociated electrolytes, such as $C_6H_5CO_2H$, are both electrically neutral, there is a major difference in the forces responsible for their formation. Simple electrostatic attractive forces between the cation and the anion hold the ion pair together, whereas a polar covalent O–H bond holds together the undissociated electrolyte.

Incomplete dissociation of a molecular solute that is miscible with water can increase the solubility of the solute.

Complex Ion Formation

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a **complex ion** (or, simply, complex), a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion {$[Cu(H_2O)_6]^{2+}$}. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure $17.5.1$. The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.



Figure $17.5.3$: The Formation of Complex Ions. An aqueous solution of $CuSO_4$ consists of hydrated Cu^{2+} ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than H_2O, replaces water molecules from the hydrated Cu^{2+} ion. For a more complete description, see www.youtube.com/watch?v=IQNcLH6OZK0.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to \(\ce{Cu^{2+}}\) for simplicity, we can write the equilibrium reactions as follows:

$$\mathrm{Cu^{2+}(aq) + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)]^{2+}_{(aq)}} \qquad K_1$$
$$\mathrm{[Cu(NH_3)]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_2]^{2+}_{(aq)}} \qquad K_2$$
$$\mathrm{[Cu(NH_3)_2]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_3]^{2+}_{(aq)}} \qquad K_3$$
$$\mathrm{[Cu(NH_3)_3]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)}} \qquad K_4$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated $\mathrm{Cu^{2+}}$ ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.

$$\mathrm{Cu^{2+}\,(aq) + 4\,NH_3\,(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}\,(aq)} \tag{17.5.3}$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant** (K_f). The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$K_\mathrm{f} = \frac{[\mathrm{[Cu(NH_3)_4]^{2+}}]}{[\mathrm{Cu^{2+}}][\mathrm{NH_3}]^4} = 2.1 \times 10^{13} = K_1K_2K_3K_4 \tag{17.5.4}$$

The formation constant (K_f) has the same general form as any other equilibrium constant expression.

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table 17.5.1.

*Table 17.5.1: Formation Constants for Selected Complex Ions in Aqueous Solution**

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \diamond [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \diamond [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \diamond [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \diamond [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \diamond [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \diamond [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \diamond [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \diamond [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \diamond [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \diamond [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \diamond [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \diamond [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}

***Reported values are overall formation constants. Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).**

	Complex Ion	Equilibrium Equation	K_f
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \diamond [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

***Reported values are overall formation constants. Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).**

Example 17.5.1

If 12.5 g of $Cu(NO_3)_2 \cdot 6H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of $Cu^{2+}(aq)$

Strategy:

A. Calculate the initial concentration of Cu^{2+} due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 17.5.3 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.
B. Substitute the final concentrations into the expression for the formation constant (Equation 17.5.4) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

Solution

Adding an ionic compound that contains Cu^{2+} to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}(aq)$, as shown in Equation 17.5.3. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of Cu^{2+} from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5 \cancel{g}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1\ mol}{295.65 \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) = 0.0846\ M$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3 required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M – 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define *x* as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is –*x*, and the change in the concentration of ammonia is +4*x*, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

Solutions to Example 17.5.1

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
change	$+x$	$+4x$	$-x$
final	x	$0.66 + 4x$	$0.0846 - x$

B Substituting the final concentrations into the expression for the formation constant (Equation 17.5.4) and assuming that $x \ll 0.0846$, which allows us to remove x from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13}$$

$$x = 2.1 \times 10^{-14}$$

The value of x indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}(aq)$ in a 1.00 M ammonia solution is therefore $2.1 \times 10^{-14} M$.

Exercise 17.5.1

The ferrocyanide ion $[Fe(CN)_6]^{4-}$ is very stable, with a $K_f = 1 \times 10^{35}$. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer available at the end of this section.

The Effect of the Formation of Complex Ions on Solubility

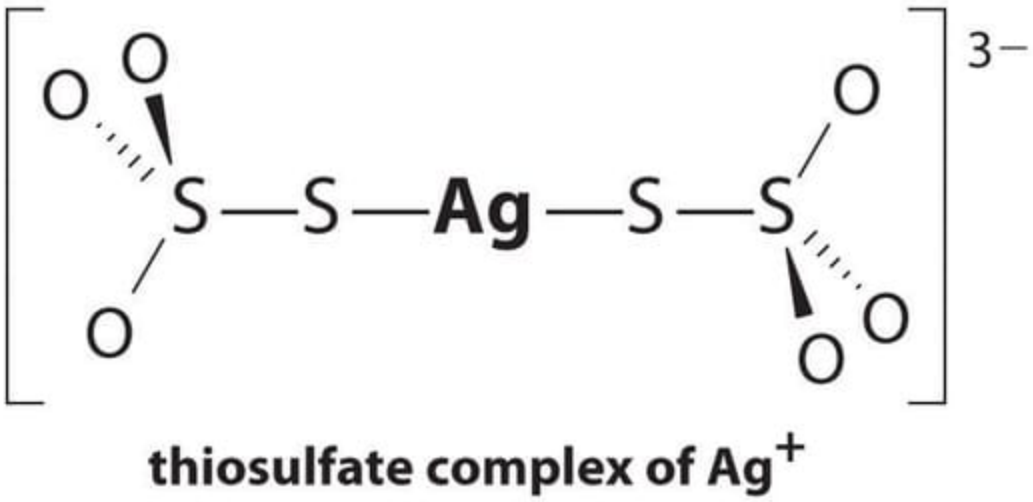
What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted $AgBr$ on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

The reaction for the dissolution of silver bromide is as follows:

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

with $K_{sp} = 5.35 \times 10^{-13}$ at 25°C.

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

$$Ag^+(aq) + 2\,S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq)$$

with $K_f = 2.9 \times 10^{13}$.

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \quad K_{sp} = 5.35 \times 10^{-13} \tag{17.5.5}$$

$$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) \quad K_f = 2.9 \times 10^{13} \tag{17.5.6}$$

$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq) \quad K = K_{sp}K_f = 15 \tag{17.5.7}$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3×10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.

Example 17.5.2

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.
B. Calculate the concentration of Ag^+ in the KCl solution.
C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

a. **A** If we let x equal the solubility of AgCl, then at equilibrium [Ag+] = [Cl^-] = x M. Substituting this value into the solubility product expression,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77 \times 10^{-10}$$
$$x = 1.33 \times 10^{-5}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

b. **B** If x equals the solubility of AgCl in the KCl solution, then at equilibrium [Ag^+] = x M and [Cl^-] = (1.0 + x) M. Substituting these values into the solubility product expression and assuming that x << 1.0,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77 \times 10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$\mathrm{AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)} \quad K_{sp} = 1.77 \times 10^{-10} \tag{17.5.8}$$
$$\mathrm{Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^-} \quad K_f = 1.1 \times 10^5 \tag{17.5.9}$$
$$\mathrm{AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^-} \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \tag{17.5.10}$$

D If we let x equal the solubility of AgCl in the KCl solution, then at equilibrium [$AgCl_2^-$] = x and [Cl^-] = 1.0 − x. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that x << 1.0,

$$K = \frac{[\mathrm{AgCl_2^-}]}{[\mathrm{Cl^-}]} = \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} = x$$

That is, AgCl dissolves in 1.0 M KCl to produce a 1.9×10^{-5} M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is 10^5 times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

Exercise 17.5.2

Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

a. pure water

b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

$$K_{sp} = 2.9 \times 10^{-29} \text{ for } HgI_2 \text{ and } K_f = 6.8 \times 10^{29} \text{ for } [HgI_4]^{2-}.$$

Answer

a. 1.9×10^{-10} M
b. 1.4 M

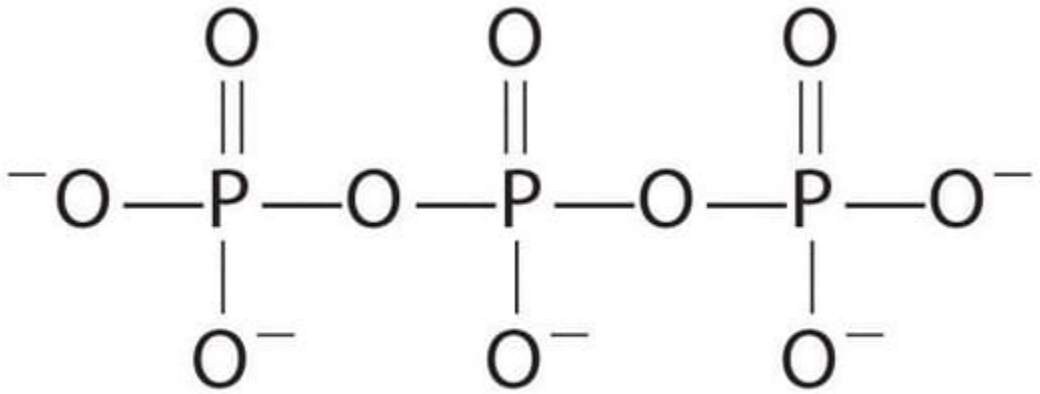
YouTube Video

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Solubility of Complex Ions: Solubility of Complex Ions(opens in new window) [youtu.be]

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in "hard" water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing. Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:



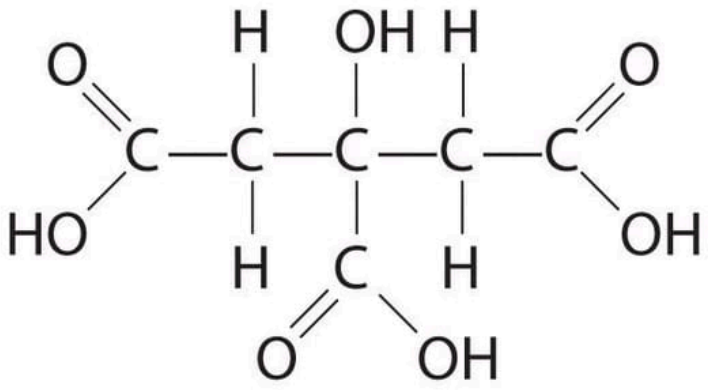
triphosphate

$$Ca^{2+}(aq) + O_3POPO_4^{4-}(aq) \rightleftharpoons [Ca(O_3POPO_3)]^{2-}(aq) \tag{17.5.11}$$

with $K_f = 4 \times 10^4$.

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. "Phosphate-free" detergents contain different kinds of complexing agents, such as

derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.



**Citric acid,
a hydroxy polycarboxylic acid**

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^1H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as “MRI contrast agents.” Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to “see” each of these separately (Figure 17.5.4). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown here.

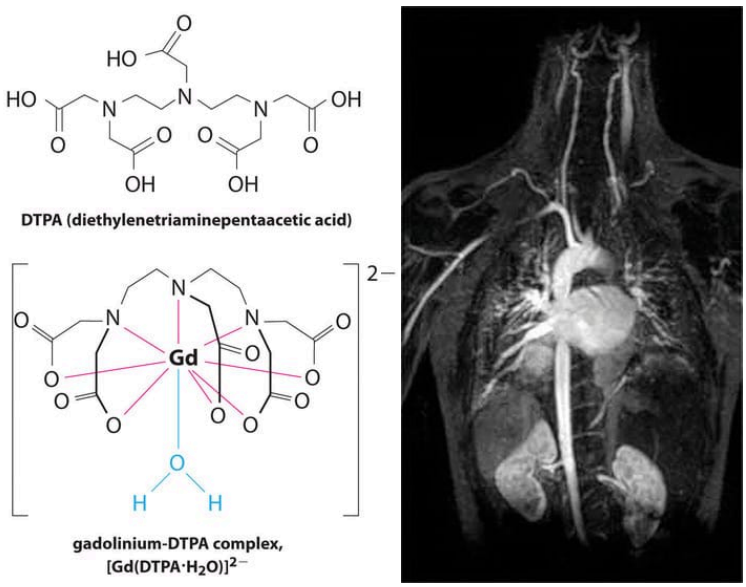


Figure 17.5.4: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Summary

Ion-pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH all affect solubility. There are four explanations why the solubility of a compound can differ from the solubility indicated by the concentrations of ions: (1) ion pair formation, in which an anion and a cation are in intimate contact in solution and not separated by solvent, (2) the incomplete dissociation of molecular solutes, (3) the formation of complex ions, and (4) changes in pH. An ion pair is held together by electrostatic attractive forces between the cation and the anion, whereas incomplete dissociation results from intramolecular forces, such as polar covalent O–H bonds.

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant (K_f). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

Answers

Exercise 17.5.1

2×10^{-6} M

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17.6: Precipitation and Separation of Ions

Learning Objectives

- Calculate ion concentrations to maintain a heterogeneous equilibrium.
- Calculate pH required to precipitate a metal hydroxide.
- Design experiments to separate metal ions in a solution of mixtures of metals.

A mixture of metal ions in a solution can be separated by precipitation with anions such as Cl^-, Br^-, $SO_4{}^{2-}$, $CO_3{}^{2-}$, S^{2-}, $Cr_2O_4{}^{2-}$, $PO_4{}^{2-}$, OH^- etc. When a metal ion or a group of metal ions form insoluble salts with a particular anion, they can be separated from others by precipitation. We can also separate the anions by precipitating them with appropriate metal ions. There are no definite dividing lines between **insoluble salts, sparingly soluble**, and **soluble salts**, but concentrations of their saturated solutions are small, medium, and large. Solubility products are usually listed for insoluble and sparingly soluble salts, but they are not given for soluble salts. Solubility products for soluble salts are very large.

What type of salts are usually soluble, sparingly soluble and insoluble? The following are some general guidelines, but these are not precise laws.

- All nitrates are soluble. The singly charged large $NO_3{}^-$ ions form salts with high solubilities. So do $ClO_4{}^-$, $ClO_3{}^-$, $NO_2{}^-$, $HCOO^-$, and CH_3COO^-.
- All chlorides, bromides, and iodides are soluble except those of Ag^+, $Hg_2{}^{2+}$, and Pb^{2+}. CaF_2, BaF_2, and PbF_2 are also insoluble.
- All sulfates are soluble, except those of Ba^{2+}, Sr^{2+}, and Pb^{2+}. The doubly charged sulfates are usually less soluble than halides and nitrates.
- Most singly charge cations K^+, Na^+, $NH_4{}^+$ form soluble salts. However, $K_3Co(NO_2)_6$ and $(NH_4)_3Co(NO_2)_6$ are insoluble.

These are handy rules for us to have if we deal with salts often. On the other hand, solubility is an important physical property of a substance, and these properties are listed in handbooks.

Chemical Separation of Metal Ions

Formation of crystals from a saturated solution is a **heterogeneous equilibrium** phenomenon, and it can be applied to separate various chemicals or ions in a solution. When solubilities of two metal salts are very different, they can be separated by precipitation. The K_{sp} values for various salts are valuable information, and some data are given in Table E3. In the first two examples, we show how barium and strontium can be separated as chromate.

Example 17.6.1

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10}. What concentration of potassium chromate will precipitate the maximum amount of either the barium or the strontium chromate from an equimolar 0.30 M solution of barium and strontium ions without precipitating the other?

Solution

Since the K_{sp} for barium chromate is smaller, we know that $BaCrO_4$ will form a precipitate first as $[CrO_4{}^{2-}]$ increases so that Q_{sp} for $BaCrO_4$ also increases from zero to K_{sp} of $BaCrO_4$, at which point, $BaCrO_4$ precipitates. As $[CrO_4{}^{2-}]$ increases, $[Ba^{2+}]$ decreases. Further increase of $[CrO_4{}^{2-}]$ till Q_{sp} for $SrCrO_4$ increases to K_{sp} of $SrCrO_4$; it then precipitates.

Let us write the equilibrium equations and data down to help us think. Let x be the concentration of chromate to precipitate Sr^{2+}, and y be that to precipitate Ba^{2+}:

$$SrCrO_4\,(s) \rightarrow Sr^{2+}\,(aq) + CrO_4{}^{2-}\,(aq)$$

According to the definition of K_{sp} we have we have $K_{sp} = (0.30)(x) = 3.6 \times 10^{-5}$. Solving for x gives

$$x = \frac{3.6 \times 10^{-5}}{0.30} = 1.2 \times 10^{-4} M$$

Further, let y be the concentration of chromate to precipitate precipitate $\mathrm{Ba^{2+}}$:

$$\mathrm{BaCrO_4\,(s)} \rightarrow \mathrm{Ba^{2+}\,(aq) + CrO_4{}^{2-}\,(aq)}$$

with $K_{sp} = (0.30)(y) = 1.2 \times 10^{-10}$. Solving for y gives

$$y = \frac{1.2 \times 10^{-10}}{0.30} = 4.0 \times 10^{-10}\ M$$

The K_{sp}'s for the two salts indicate $\mathrm{BaCrO_4}$ to be much less soluble, and it will precipitate before any $\mathrm{SrCrO_4}$ precipitates. If chromate concentration is maintained less than $1.2 \times 10^{-4} M$, then all $\mathrm{Sr^{2+}}$ ions will remain in the solution.

Discussion

In reality, controling the increase of $[\mathrm{CrO_4{}^{2-}}]$ is very difficult.

Example 17.6.2

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10}. Potassium chromate is added a small amount at a time to first precipitate $\mathrm{BaCrO_4}$. Calculate $[\mathrm{Ba^{2+}}]$ when the first trace of $\mathrm{SrCrO_4}$ precipitate starts to form in a solution that contains 0.30 M each of $\mathrm{Ba^{2+}}$ and $\mathrm{Sr^{2+}}$ ions.

Solution

From the solution given in Example 17.6.1, $[\mathrm{CrO_4{}^{2-}}] = 3.6 \times 10^{-4}\ M$ when $\mathrm{SrCrO_4}$ starts to form. At this concentration, the $[\mathrm{Ba^{2+}}]$ is estimated at $3.6 \times 10^{-4} = 1.2 \times 10^{-10}$.

The K_{sp} of $\mathrm{BaCrO_4}$.

Thus,

$$[\mathrm{Ba^{2+}}] = 3.33 \times 10^{-7}\ M$$

Very small indeed, compared to 0.30. In the fresh precipitate of $\mathrm{SrCrO_4}$, the molar ratio of $\mathrm{SrCrO_4}$ to $\mathrm{BaCrO_4}$ is

$$\frac{0.30}{3.33 \times 10^{-7}} = 9.0 \times 10^{5}.$$

Hence, the amount of $\mathrm{Ba^{2+}}$ ion in the solid is only 1×10^{-6} (i.e., 1 ppm) of all metal ions, providing that all the solid was removed when

$$[\mathrm{CrO_4{}^{2-}}] = 3.6 \times 10^{-4} M.$$

Discussion

The calculation shown here indicates that the separation of Sr and Ba is pretty good. In practice, an impurity level of 1 ppm is a very small value.

Example 17.6.3

What reagent should you use to separate silver and lead ions that are present in a solution? What data or information will be required for this task?

Solution

The K_{sp}'s for salts of silver and lead are required. We list the K_{sp}'s for chlorides and sulfates in a table here. These value are found in the Handbook Menu of our website as Salts K_{sp}.

Solutions to Example 17.6.3

Salt	K_{sp}	Salt	K_{sp}
$AgCl$	1.8×10^{-10}	Ag_2SO_4	1.4×10^{-5}
Hg_2Cl_2	1.3×10^{-18}	$BaSO_4$	1.1×10^{-10}
$PbCl_2$	1.7×10^{-5}	$CaSO_4$	2.4×10^{-5}
		$PbSO_4$	6.3×10^{-7}
		$SrSO_4$	3.2×10^{-7}

Because the K_{sp}'s $AgCl$ and $PbCl_2$ are very different, chloride, Cl^-, apppears a good choice of negative ions for their separation.

The literature also indicates that $PbCl_2$ is rather soluble in warm water, and by heating the solution to 350 K (80°C), you can keep Pb^{2+} ions in solution and precipitate $AgCl$ as a solid. The solubility of $AgCl$ is very small even at high temperatures.

Discussion

Find more detailed information about the solubility of lead chloride as a function of temperature.

Can sulfate be used to separate silver and lead ions? Which one will form a precipitate first as the sulfate ion concentration increases? What is the $[Pb^{2+}]$ when Ag_2SO_4 begins to precipitate in a solution that contains 0.10 M Ag^+?

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

The Separation of Two Ions by a Difference in Solubility: The Separation of Two Ions by a Difference in Solubility(opens in new window) [youtu.be]

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17.7: Qualitative Analysis for Metallic Elements

Learning Objectives

- To know how to separate metal ions by selective precipitation.
- To understand how several common metal cations can be identified in a solution using selective precipitation.

The composition of relatively complex mixtures of metal ions can be determined using **qualitative analysis**, a procedure for discovering the identity of metal ions present in the mixture (rather than quantitative information about their amounts). The procedure used to separate and identify more than 20 common metal cations from a single solution consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all of the metal ions are precipitated, as illustrated in Figure 17.7.1.

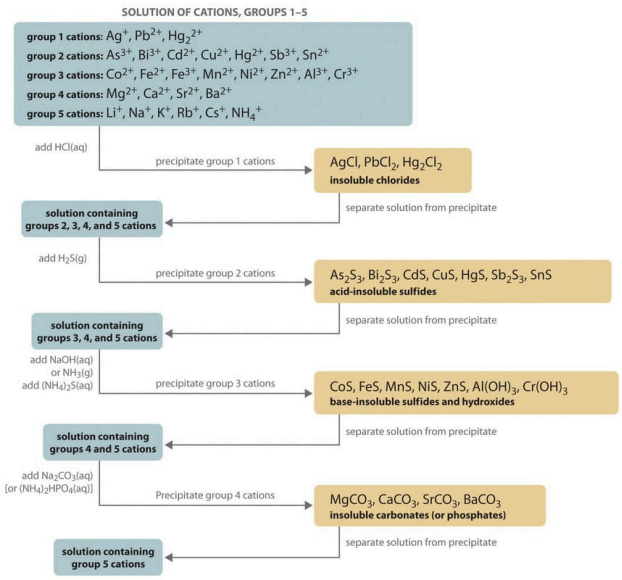


Figure 17.7.1: Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

Group 1: Insoluble Chlorides

Most metal chloride salts are soluble in water; only $\mathrm{Ag^+}$, $\mathrm{Pb^{2+}}$, and $\mathrm{Hg_2{}^{2+}}$ form chlorides that precipitate from water. Thus the first step in a qualitative analysis is to add about 6 M HCl, thereby causing AgCl, $\mathrm{PbCl_2}$, and/or $\mathrm{Hg_2Cl_2}$ to precipitate. If no precipitate forms, then these cations are not present in significant amounts. The precipitate can be collected by filtration or centrifugation.

Group 2: Acid-Insoluble Sulfides

Next, the acidic solution is saturated with $\mathrm{H_2S}$ gas. Only those metal ions that form very insoluble sulfides, such as $\mathrm{As^{3+}}$, $\mathrm{Bi^{3+}}$, $\mathrm{Cd^{2+}}$, $\mathrm{Cu^{2+}}$, $\mathrm{Hg^{2+}}$, $\mathrm{Sb^{3+}}$, and $\mathrm{Sn^{2+}}$, precipitate as their sulfide salts under these acidic conditions. All others, such as $\mathrm{Fe^{2+}}$ and $\mathrm{Zn^{2+}}$, remain in solution. Once again, the precipitates are collected by filtration or centrifugation.

Group 3: Base-Insoluble Sulfides (and Hydroxides)

Ammonia or NaOH is now added to the solution until it is basic, and then $\mathrm{(NH_4)_2S}$ is added. This treatment removes any remaining cations that form insoluble hydroxides or sulfides. The divalent metal ions $\mathrm{Co^{2+}}$, $\mathrm{Fe^{2+}}$, $\mathrm{Mn^{2+}}$, $\mathrm{Ni^{2+}}$, and $\mathrm{Zn^{2+}}$ precipitate as their sulfides, and the trivalent metal ions $\mathrm{Al^{3+}}$ and $\mathrm{Cr^{3+}}$ precipitate as their hydroxides: $\mathrm{Al(OH)_3}$ and $\mathrm{Cr(OH)_3}$. If the mixture contains $\mathrm{Fe^{3+}}$, sulfide reduces the cation to $\mathrm{Fe^{2+}}$, which precipitates as FeS.

Group 4: Insoluble Carbonates or Phosphates

The next metal ions to be removed from solution are those that form insoluble carbonates and phosphates. When $\mathrm{Na_2CO_3}$ is added to the basic solution that remains after the precipitated metal ions are removed, insoluble carbonates precipitate and are collected. Alternatively, adding $\mathrm{(NH_4)_2HPO_4}$ causes the same metal ions to precipitate as insoluble phosphates.

Group 5: Alkali Metals

At this point, we have removed all the metal ions that form water-insoluble chlorides, sulfides, carbonates, or phosphates. The only common ions that might remain are any alkali metals ($\mathrm{Li^+}$, $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Rb^+}$, and $\mathrm{Cs^+}$) and ammonium ($\mathrm{NH_4{}^+}$). We now take a second sample from the original solution and add a small amount of NaOH to neutralize the ammonium ion and produce $\mathrm{NH_3}$. (We cannot use the same sample we used for the first four groups because we added ammonium to that sample in earlier steps.) Any ammonia produced can be detected by either its odor or a litmus paper test. A flame test on another original sample is used to detect sodium, which produces a characteristic bright yellow color. The other alkali metal ions also give characteristic colors in flame tests, which allows them to be identified if only one is present.

Metal ions that precipitate together are separated by various additional techniques, such as forming complex ions, changing the pH of the solution, or increasing the temperature to redissolve some of the solids. For example, the precipitated metal chlorides of group 1 cations, containing $\mathrm{Ag^+}$, $\mathrm{Pb^{2+}}$, and $\mathrm{Hg_2{}^{2+}}$, are all quite insoluble in water. Because $\mathrm{PbCl_2}$ is much more soluble in hot water than are the other two chloride salts, however, adding water to the precipitate and heating the resulting slurry will dissolve any $\mathrm{PbCl_2}$ present. Isolating the solution and adding a small amount of $\mathrm{Na_2CrO_4}$ solution to it will produce a bright yellow precipitate of $\mathrm{PbCrO_4}$ if $\mathrm{Pb^{2+}}$ were in the original sample (Figure 17.7.2).



Figure 17.7.2: When a small amount of $\mathrm{Na_2CrO_4}$ solution is added to a sample containing $\mathrm{Pb^{2+}}$ ions in water, a bright yellow precipitate of $\mathrm{PbCrO_4}$ forms. (CC BY-SA 3.0 Unported; PRHaney via Wikipedia).

As another example, treating the precipitates from group 1 cations with aqueous ammonia will dissolve any AgCl because $\mathrm{Ag^+}$ forms a stable complex with ammonia: $\mathrm{[Ag(NH_3)_2]^+}$. In addition, $\mathrm{Hg_2Cl_2}$ disproportionates in ammonia.

$$\mathrm{2\,Hg_2{}^{2+} \rightarrow Hg + Hg^{2+}}$$

to form a black solid that is a mixture of finely divided metallic mercury and an insoluble mercury(II) compound, which is separated from solution:

$$\mathrm{Hg_2Cl_2\,(s) + 2\,NH_3\,(aq) \rightarrow Hg\,(l) + Hg(NH_2)Cl\,(s) + NH_4^+\,(aq) + Cl^-\,(aq)}$$

Any silver ion in the solution is then detected by adding HCl, which reverses the reaction and gives a precipitate of white AgCl that slowly darkens when exposed to light:

$$[\mathrm{Ag(NH_3)_2}]^+(\mathrm{aq}) + 2\,\mathrm{H}^+(\mathrm{aq}) + \mathrm{Cl}^-(\mathrm{aq}) \rightarrow \mathrm{AgCl(s)} + 2\,\mathrm{NH_4^+(aq)}$$

Similar but slightly more complex reactions are also used to separate and identify the individual components of the other groups.

Summary

In qualitative analysis, the identity, not the amount, of metal ions present in a mixture is determined. The technique consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all the metal ions are precipitated. Other additional steps are needed to separate metal ions that precipitate together.

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17.E: Additional Aspects of Aqueous Equilibria (Exercises)

17.1: The Common-Ion Effect

17.2: Buffered Solutions

Conceptual Problems

1. Explain why buffers are crucial for the proper functioning of biological systems.

2. What is the role of a buffer in chemistry and biology? Is it correct to say that buffers prevent a change in $[H_3O^+]$? Explain your reasoning.

3. Explain why the most effective buffers are those that contain approximately equal amounts of the weak acid and its conjugate base.

4. Which region of the titration curve of a weak acid or a weak base corresponds to the region of the smallest change in pH per amount of added strong acid or strong base?

5. If you were given a solution of sodium acetate, describe two ways you could convert the solution to a buffer.

6. Why are buffers usually used only within approximately one pH unit of the pK_a or pK_b of the parent weak acid or base?

7. The titration curve for a monoprotic acid can be divided into four regions: the starting point, the region around the midpoint of the titration, the equivalence point, and the region after the equivalence point. For which region would you use each approach to describe the behavior of the solution?

a. a buffer
b. a solution of a salt of a weak base
c. a solution of a weak acid
d. diluting a strong base

8. Which of the following will produce a buffer solution? Explain your reasoning in each case.

a. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
b. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
c. mixing 100 mL of 0.1 M hydrofluoric acid and 100 mL of 0.1 M HCl
d. mixing 100 mL of 0.1 M hydrofluoric acid and 50 mL of 0.1 M $NaOH$
e. mixing 100 mL of 0.1 M sodium fluoride and 50 mL of 0.1 M $NaOH$.

9. Which of the following will produce a buffer solution? Explain your reasoning in each case.

a. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
b. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
c. mixing 100 mL of 0.1 M acetic acid and 100 mL of 0.1 M $NaOH$
d. mixing 100 mL of 0.1 M acetic acid and 50 mL of 0.1 M $NaOH$
e. mixing 100 mL of 0.1 M sodium acetate and 50 mL of 0.1 M acetic acid

10. Use the definition of Kb for a weak base to derive the following expression, which is analogous to the Henderson-Hasselbalch approximation but for a weak base (B) rather than a weak acid (HA):

$$pOH = pK_b - \log\left(\frac{[base]}{[acid]}\right) \tag{17.E.1}$$

11. Why do biological systems use overlapping buffer systems to maintain a constant pH?

12. The CO_2/HCO_3^- buffer system of blood has an effective pK_a of approximately 6.1, yet the normal pH of blood is 7.4. Why is CO_2/HCO_3^- an effective buffer when the pK_a is more than 1 unit below the pH of blood? What happens to the pH of blood when the CO_2 pressure increases? when the O_2 pressure increases?

13. Carbon dioxide produced during respiration is converted to carbonic acid (H_2CO_3). The pK_a1 of carbonic acid is 6.35, and its pK_a2 is 10.33. Write the equations corresponding to each pK value and predict the equilibrium position for each reaction.

Answer

1. Buffers are crucial for the proper function of biological systems because they help maintain a relatively constant pH that maintains homeostasis and this is required for bodily function. For example, buffers can prevent stomach acid from being too acidic in which tissues and other parts of the body would be harmed.

2. The role of a buffer in chemistry and biology is to resist pH changes upon the addition of an acid or base. It is correct to say that buffers prevent a change in hydronium ion concentration because the pH is a measure of the acidity or alkalinity of a solution.

3. The most effective buffers are those that contain approximately equal amounts of the weak acid and its conjugate base because when placed in the Henderson-Hasselbalch equation the pH approximately equals the pK_a. This is the goal because the more the ratio needs to differ to achieve the desired pH, the less effective the buffer and it should not differ by more than tenfold.

4. The region after the equivalence point on a titration curve of a weak acid or a weak base corresponds to the smallest change in pH per amount of added strong acid or strong base. This is because the strong acid or strong base completely neutralized the weak acid or weak base in which the pH remains constant relative to the strong acid or strong base.

5. Sodium acetate is a salt, therefore it can't be regarded as an acid or a base. One way to convert the solution to a buffer is to combine sodium acetate with a weak acid such as acetic acid. The sodium acetate would react with the hydronium ions and the acetic acid would react with hydroxide ions to prevent drastic changes in pH. Another way to convert the solution to a buffer is by titrating a weak acid and strong base or strong base and weak acid. For example, combining acetic acid to sodium hydroxide to produce sodium acetate (a neutralization reaction).

6.

Buffers are usually used only within approximately one pH unit of the pK_a or pK_b of the parent weak acid or base because the ability of a buffer solution to maintain a nearly constant pH due to a small amount of acid or base is greatest at the pK_a and decreases as the pH of the solution goes above or below the pK_a.

$pH = pK_a + log(\frac{[B]}{[A]})$

When $\frac{[B]}{[A]} = 10$: $pH = pK_a + 1$

When $\frac{[B]}{[A]} = \frac{1}{10}$: $pH = pK_a - 1$

7.

a. I would use the region around the midpoint of the titration to describe the behavior of a buffer because the midpoint of the titration is defined as the point at which exactly enough acid or base has been added to neutralize one-half of the acid or the base originally present while maintaining a relatively constant pH.

b. I would use the equivalence point region to describe the behavior of a solution of a salt of a weak base because at this point the amount of titrant added is enough to completely neutralize the solution.

c. I would use the starting point region of the titration curve to describe the behavior of the solution of a weak acid because it is expected to be at a higher pH than a strong acid but lower than pH 7.

d. I would use the region after the equivalence point to describe the dilution of a strong base because in this region one can

predict the pH by simply taking into account the amount of excess base.

8.

a. This will not produce a buffer solution because the hydrochloric acid completely neutralizes the sodium fluoride to give sodium chloride.

b. This will produce a buffer solution because the hydrochloric acid neutralizes only half of the acetic acid to give a solution containing equal amounts of hydrofluoric acid and sodium chloride.

c. This will not produce a buffer solution because hydrofluoric acid is a weak acid and hydrochloric acid is a strong acid.

d. This will produce a buffer solution because the solution will contain a 2:1 ratio of hydrofluoric acid and sodium hydroxide.

e. This will not produce a buffer solution solution because sodium fluoride is a weak base and sodium hydroxide is a strong base.

9.

a. This will not produce a buffer because the hydrochloric acid completely neutralizes the sodium acetate to give acetic acid and sodium chloride.

b. This will produce a buffer because the HCl neutralizes only half of the sodium acetate to give a solution containing equal amounts of acetic acid and sodium acetate.

c. This will not produce a buffer because the sodium hydroxide completely neutralizes the acetic acid to give sodium acetate.

d. This will produce a buffer because the sodium hydroxide neutralizes only half of the acetic acid to give a solution containing equal amounts of acetic acid and sodium acetate.

e. This will produce a buffer because the solution will contain a 2:1 ratio of sodium acetate and acetic acid.

10.

For pH:

$HA \overset{K_a}{\rightleftharpoons} A^- + H^+$

$K_a = \frac{[H^+][A^-]}{[HA]}$

$log(K_a) = log([H^+]) + log(\frac{[A^-]}{[HA]})$

$-pK_a = -pH + log(\frac{[A^-]}{[HA]})$

$pH = pK_a + log(\frac{[A^-]}{[HA]})$

For pOH:

$A^- \overset{K_b}{\rightleftharpoons} HA + OH^-$

$K_b = \frac{[HA][OH^-]}{[A^-]}$

$log(K_b) = log([OH^-]) + log(\frac{[HA]}{[A^-]})$

$-pK_b = -pOH - log(\frac{[A^-]}{[HA]})$

$pOH = pK_b - log(\frac{[A^-]}{[HA]})$

Helpful Equations:

$pK_a = -log(K_a) \rightarrow -pK_a = log(K_a)$

$-log([H^+]) = pH \rightarrow log([H^+]) = -pH$

$pK_b = -log(K_b) \rightarrow -pK_a = log(K_b)$

$-log([OH^-]) = pOH \rightarrow log([OH^-]) = -pOH$

11. Biological systems use overlapping buffer systems to maintain a constant pH because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4.

12. CO_2/HCO_3^- is an effective buffer when the pK_a is more than 1 unit below the pH of blood because the kidneys help control acid-base balance by excreting hydrogen ions and generating bicarbonate that helps maintain blood plasma pH within the normal range. The bicarbonate ion can combine with a proton to form carbonic acid and the more protons are absorbed from the solution the more the pH increases, resulting in hemoglobin absorbing oxygen. Carbonic acid, which can be formed from carbon dioxide and water, can dissociate into a proton and bicarbonate ion which increases the hydrogen ion concentration and lowers the blood pH, resulting in hemoglobin proteins releasing oxygen. The carbonic acid, which can be formed from bicarbonate, is converted to carbon dioxide and water via a very fast enzymatic reaction. Carbon dioxide, being volatile, can be rapidly expelled from the body at varying rates by respiration.

13.

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \; pK_{a1} = 6.35$ left

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \; pK_{a2} = 10.33$ right

Numerical Problems

1.Benzenesulfonic acid ($pKa = 0.70$) is synthesized by treating benzene with concentrated sulfuric acid. Calculate the following:

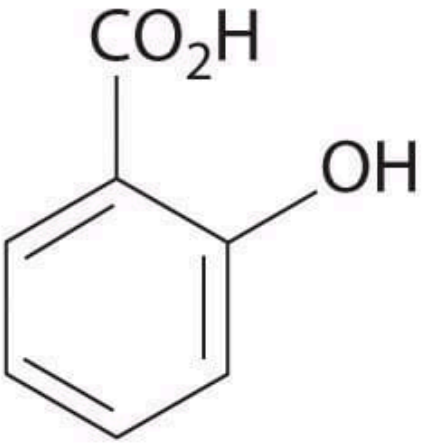
a. the pH of a 0.286 M solution of benzenesulfonic acid
b. the pH after adding enough sodium benzenesulfonate to give a final benzenesulfonate concentration of 0.100 M

2. Phenol has a pK_a of 9.99. Calculate the following:

a. the pH of a 0.195 M solution
b. the percent increase in the concentration of phenol after adding enough solid sodium phenoxide (the sodium salt of the conjugate base) to give a total phenoxide concentration of 0.100 M

3. Salicylic acid is used in the synthesis of acetylsalicylic acid, or aspirin. One gram dissolves in 460 mL of water to create a saturated solution with a pH of 2.40.

a. What is the K_a of salicylic acid?
b. What is the final pH of a saturated solution that is also 0.238 M in sodium salicylate?
c. What is the final pH if 10.00 mL of 0.100 M HCl are added to 150.0 mL of the buffered solution?
d. What is the final pH if 10.00 mL of 0.100 M NaOH are added to 150.0 mL of the buffered solution?



salicylic acid

4. An intermediate used in the synthesis of perfumes is valeric acid, also called pentanoic acid. The pK_a of pentanoic acid is 4.84 at 25°C.

a. What is the pH of a 0.259 M solution of pentanoic acid?
b. Sodium pentanoate is added to make a buffered solution. What is the pH of the solution if it is 0.210 M in sodium pentanoate?
c. What is the final pH if 8.00 mL of 0.100 M HCl are added to 75.0 mL of the buffered solution?
d. What is the final pH if 8.00 mL of 0.100 M NaOH are added to 75.0 mL of the buffered solution?

Answer

1.

a. $pH = -log([H^+]) = -log(0.2388) = 0.62$

$$K_a = \frac{[H^+][A^-]}{[HA]} \rightarrow K_a = \frac{[H^+]^2}{[HA]} \rightarrow [H^+] = \sqrt{K_a \times [HA]} = \sqrt{10^{-0.70} \times 0.286\,M} = 0.2388$$

b. $pH = -log([H^+]) = -log(0.14125) = 0.850$

$$K_a = \frac{[H^+][A^-]}{[HA]} \rightarrow K_a = \frac{[H^+]^2}{[HA]} \rightarrow [H^+] = \sqrt{K_a \times [HA]} = \sqrt{10^{-0.70} \times 0.100\,M} = 0.14125$$

2.

a. $pH = -log(4.46 \times 10^{-6}) = 5.35$

$K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]} = \frac{x^2}{0.195} \rightarrow 10^{-9.99} = \frac{x^2}{0.195} \rightarrow x = 4.46 \times 10^{-6}$

$Assumption\ Valid: \frac{4.46 \times 10^{-6}}{0.195\,M} \times 100\% < 5\%$

	C_6H_5OH	H_2O	$C_6H_5O^-$	H_3O^+
I	0.195	-	0	0

C	-x	-	+x	+x
E	0.195-x	-	x	x

b. $Percent\ \ increase = \frac{3.20\times10^{-6}}{4.46\times10^{-6}} x100\% = 71.6\%$

$K_a = \frac{[C_6H_5O^-][H_3O^+]}{C_6H_5OH} = \frac{x^2}{0.100} \rightarrow 10^{-9.99} = \frac{x^2}{0.100} \rightarrow x = 3.20 \times 10^{-6}$

3.

a. $K_a = \frac{[C_9H_8O_4][H_3O^+]}{[C_7H_6O_3]} = \frac{x^2}{0.015739} \rightarrow \frac{(3.98\times10^{-3})^2}{0.015739} = 1.0 \times 10^{-3}$

$C_7H_6O_3 : 1\ g \times \frac{1\ mol}{138.121\ g\ mol} \times \frac{1}{460\ mL \times \frac{1\ L}{1000\ mL}} = 0.015739\ M$

$pH = -log([H^+]) \rightarrow [H^+] = 10^{-pH} = 10^{-2.40} = 3.98 \times 10^{-3}$

b. $pH = pK_a + log(\frac{[C_7H_5NaO_3]}{[C_7H_6O_3]}) = -log(1.01 \times 10^{-3}) + log(\frac{0.238}{0.015739}) = 4.17$

c. $pH = pK_a + log(\frac{mol\ C_7H_5NaO_3 - mol\ HCl}{mol\ C_9H_8O_4 + mol\ HCl}) = -log(1.01 \times 10^{-3}) + log(\frac{0.0357-0.001}{0.00236085+0.001}) = 4.01$

$HCl : .01\ L \times 0.100\ M = 0.001\ mol$

$C_7H_5NaO_3 : 0.15\ L \times 0.238\ M = 0.0357\ mol$

$C_7H_6O_3 : 0.15\ L \times 0.015739\ M = 0.00236085\ mol$

d. $pH = pK_a + log(\frac{mol\ C_7H_5NaO_3 + mol\ NaOH}{mol\ C_9H_8O_4 - mol\ NaOH}) = -log(1.01 \times 10^{-3}) + log(\frac{0.0357+0.001}{0.00236085-0.001}) = 4.43$

$NaOH : .01\ L \times 0.100\ M = 0.001\ mol$

$C_7H_5NaO_3 : 0.15\ L \times 0.238\ M = 0.0357\ mol$

$C_7H_6O_3 : 0.15\ L \times 0.015739\ M = 0.00236085\ mol$

4.

a. $pH = -log([H^+]) = -log(3.7 \times 10^{-6}) = 5.43$

$K_a = \frac{[H^+][A^-]}{[HA]} \rightarrow K_a = \frac{[H^+]^2}{[HA]} \rightarrow [H^+] = \sqrt{K_a \times [HA]} = \sqrt{10^{-4.84} \times 0.259\ M} = 3.7 \times 10^{-6}$

b. $pH = pK_a + log(\frac{B}{A}) = 4.84 + log(\frac{0.210}{0.259}) = 4.75$

c. $pH = pK_a + log(\frac{B}{A}) = 4.84 + log(\frac{mol\ C_5H_9NaO_2 - mol\ HCl}{mol\ C_5H_{10}O_2 + mol\ HCl}) = 4.84 + log(\frac{0.01575-8\times10^{-4}}{0.019425+8\times10^{-4}}) = 4.71$

$HCl : 8.00\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.100\ M = 8 \times 10^{-4}\ mol$

$C_5H_9NaO_2 : 75.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.210\ M = 0.01575\ mol$

$C_5H_{10}O_2 : 75.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.259\ M = 0.019425\ mol$

d. $pH = pK_a + log(\frac{B}{A}) = 4.84 + log(\frac{mol\ C_5H_9NaO_2 + mol\ NaOH}{mol\ C_5H_{10}O_2 - mol\ NaOH}) = 4.84 + log(\frac{0.01575+8\times10^{-4}}{0.019425-8\times10^{-4}}) = 6.07$

$NaOH : 8.00\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.100\ M = 8 \times 10^{-4}\ mol$

$C_5H_9NaO_2 : 75.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.210\ M = 0.01575\ mol$

$C_5H_{10}O_2 : 75.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.259\ M = 0.019425\ mol$

17.3: Acid-Base Titrations

Conceptual Problems

1. Why is the portion of the titration curve that lies below the equivalence point of a solution of a weak acid displaced upward relative to the titration curve of a strong acid? How are the slopes of the curves different at the equivalence point? Why?

2. Predict whether each solution will be neutral, basic, or acidic at the equivalence point of each titration.

a. An aqueous solution of $NaOH$ is titrated with 0.100 M HCl.
b. An aqueous solution of ethylamine ($CH_3CH_2NH_2$) is titrated with 0.150 M HNO_3
c. An aqueous solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) is titrated with 0.050 M KOH.

3. The pKa values of phenol red, bromophenol blue, and phenolphthalein are 7.4, 4.1, and 9.5, respectively. Which indicator is best suited for each acid–base titration?

a. titrating a solution of $Ba(OH)_2$ with 0.100 M HCl
b. titrating a solution of trimethylamine (Me_3N) with 0.150 M HNO_3
c. titrating a solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) with 0.050 M KOH

4. For the titration of any strong acid with any strong base, the pH at the equivalence point is 7.0. Why is this not usually the case in titrations of weak acids or weak bases?

5. Why are the titration curves for a strong acid with a strong base and a weak acid with a strong base identical in shape above the equivalence points but not below?

6. Describe what is occurring on a molecular level during the titration of a weak acid, such as acetic acid, with a strong base, such as $NaOH$, at the following points along the titration curve. Which of these points corresponds to $pH = pK_a$?

a. at the beginning of the titration
b. at the midpoint of the titration
c. at the equivalence point
d. when excess titrant has been added

7. On a molecular level, describe what is happening during the titration of a weak base, such as ammonia, with a strong acid, such as HCl, at the following points along the titration curve. Which of these points corresponds to $pOH = pK_b$?

a. at the beginning of the titration
b. at the midpoint of the titration
c. at the equivalence point
d. when excess titrant has been added

8. For the titration of a weak acid with a strong base, use the K_a expression to show that $pH = pK_a$ at the midpoint of the titration.

9. Chemical indicators can be used to monitor pH rapidly and inexpensively. Nevertheless, electronic methods are generally preferred. Why?

10. Why does adding ammonium chloride to a solution of ammonia in water decrease the pH of the solution?

11. Given the equilibrium system $CH_3CO_2H\ (aq) \rightleftharpoons CH_3CO_2^-\ (aq) + H^+\ (aq)$, explain what happens to the position of the equilibrium and the pH in each case.

a. Dilute HCl is added.
b. Dilute $NaOH$ is added.

c. Solid sodium acetate is added.

12. Given the equilibrium system $CH_3NH_2\ (aq) + H_2O\ (l) \rightleftharpoons CH_3NH_3^+\ (aq) + OH^-\ (aq)$, explain what happens to the position of the equilibrium and the pH in each case.

a. Dilute HCl is added.
b. Dilute $NaOH$ is added.
c. Solid $CH_3NH_3^+Cl^-$ is added.

Answers

1. The portion of the titration curve that lies below the equivalence point of a solution of a weak acid is displaced upward relative to the titration curve of a strong acid because the starting point of a weak acid is at a higher pH compared to that of a strong acid. The slope for a strong acid is greater compared to that of a weak acid because when a weak acid is neutralized, the solution that remains is basic because the acid's conjugate base remains in solution.

2.

a. The solution will be neutral at the equivalence point because sodium hydroxide is a strong base and hydrochloric acid is a strong acid.

b. The solution will be acidic at the equivalence point because ethylamine is a weak base and nitric acid is a strong acid.

c. The solution will be basic at the equivalence point because aniline hydrochloride is a weak acid and potassium hydroxide is a strong base.

3.

a. Barium hydroxide is a strong base and hydrochloric acid is a strong acid thus phenol red with the $pK_a = 7.4$ is best suited for the reaction.

b. Trimethylamine is a weak base and nitric acid is a strong acid thus bromophenol blue with the $pK_a = 4.1$ is best suited for the reaction.

c. Aniline hydrochloride is a weak acid and potassium hydroxide is a strong base thus phenolphthalein with $pK_a = 9.5$ is best suited for the reaction.

4. This is not usually the case in the titration of weak acids and weak bases because weak acids and weak bases would only ionize partially, thus complete neutralization does not occur.

5. The titration curve for a strong acid with a strong base is identical in shape above the equivalence point of the titration curve with a weak acid and strong base because both cases involve the addition of strong base. Not only does the strong base completely neutralize the acid but there is an excess of a strong base that makes the solution basic.

6.

a. The titration begins with a pH is higher than the titration of a strong acid. At the beginning of the titration, there is a sharp increase in pH because the anion of the weak acid becomes a common ion that reduces the ionization of the acid.

b. There is a sharp increase at the beginning of the titration that changes gradually due to the solution becoming a buffer. This continues until the strong base has overcome the buffer capacity. At the midpoint of the titration, the concentration of the weak acid is equal to the concentration of its conjugate base. This point is also known as half-neutralization because half the acid has been neutralized by the strong base.

c. At the equivalence point the pH is greater than 7 because the acid (HA) has been converted to its conjugate base (A^-) by sodium hydroxide and equilibrium moves backward toward the acid and produces hydroxide:

$A^- + H_2O \rightleftharpoons AH + OH^-$

d. When the excess titrant has been added the solution becomes basic because sodium hydroxide completely neutralized the weak acid.

7.

a. The titration begins with a pH that is lower than the titration of a strong base but higher than the $pH = 7$. At the beginning of the titration, there is a sharp decrease in pH because the cation of the weak base becomes a common ion that reduces the ionization of the base.

b. The sharp decrease at the beginning of the titration changes gradually due to the solution becoming a buffer. This continues until the strong acid has overcome the buffer capacity. At the midpoint of the titration, the concentration of the weak base is equal to the concentration of its conjugate acid $pH = pK_a$. This point is also known as half-neutralization because half the base has been neutralized by the strong acid.

c. At the equivalence point the pH is less than 7 because the base NH_3 has been converted to its conjugate acid NH_4^+ by hydrochloric acid and equilibrium moves forwards toward the base and produces NH_4Cl^-:

$$NH_3 + HCl \rightleftharpoons NH_4Cl$$

d. When excess titrant has been added the solution becomes acidic because hydrochloric acid completely neutralized the weak base.

8.

$$HA \overset{K_a}{\rightleftharpoons} A^- + H^+$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pH = pK_a + log(\frac{[A^-]}{[HA]}$$

Assume $[A^-] = [HA] = 1$

$$pH = pK_a + log(1)$$

$$pH = pK_a + 0$$

$$pH = pK_a$$

9. Electronic methods are preferred over chemical indicators because it is a more accurate method at determining the pH. Also, chemical indicators must be selected to observe a narrow pH range while electronic methods observe a wider range.

10.

Ammonia is a weak base and dissociates in water as:

$$NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

When NH_4Cl is added, it 100% dissociates into NH_4^+ and Cl^- in water:

$$NH_4Cl\ (aq) \rightleftharpoons NH_4^+\ (aq) + Cl^-\ (aq)$$

Due to common ion, $NH_4^+\ (aq)$ the dissociation of NH_3 will decrease. Thus, the concentration of $OH^-\ (aq)$ decreases and the concentration of H_3O^+ increases.

Since $pH = -log(H_3O^+)$ the pH and H_3O^+ are inversely related, the concentration of H_3O^+ concentration increases and pH decreases.

11.

a. The position of equilibrium shift to the left and the pH decreases.

b. The position of equilibrium shifts to the right and the pH increases.

c. The position of equilibrium shifts to the left and the pH increases.

12.

a. The position of equilibrium shifts to the left and the pH decreases.

b. The position of equilibrium shifts to the left and the pH increases.

c. The position of equilibrium shifts to the left and the pH increases.

Numerical Problems

1. Calculate the pH of each solution.

a. A volume of 25.0 mL of 6.09 M HCl is added to 100.0 mL of distilled water
b. A volume of 5.0 mL of 2.55 M $NaOH$ is added to 75.0 mL of distilled water.

2. What is the pH of a solution prepared by mixing 50.0 mL of 0.225 M HCl with 100.0 mL of a 0.184 M solution of $NaOH$?

3. What volume of 0.50 M HCl is needed to completely neutralize 25.00 mL of 0.86 M $NaOH$?

4.Calculate the final pH when each pair of solutions is mixed.

a. 100 mL of 0.105 M HCl and 100 mL of 0.115 M sodium acetate
b. 50 mL of 0.10 M HCl and 100 mL of 0.15 M sodium acetate
c. 100 mL of 0.109 M acetic acid and 100 mL of 0.118 M $NaOH$
d. 100 mL of 0.998 M acetic acid and 50.0 mL of 0.110 M $NaOH$

5. Calculate the final pH when each pair of solutions is mixed.

a. 100 mL of 0.983 M HCl and 100 mL of 0.102 M sodium fluoride
b. 50.0 mL of 0.115 M HCl and 100 mL of 0.109 M sodium fluoride
c. 100 mL of 0.106 M hydrofluoric acid and 50.0 mL of 0.996 M $NaOH$
d. 100 mL of 0.107 M sodium acetate and 50.0 mL of 0.987 M acetic acid

6. Calcium carbonate is a major contributor to the “hardness” of water. The amount of CaCO3 in a water sample can be determined by titrating the sample with an acid, such as HCl, which produces water and CO2. Write a balanced chemical equation for this reaction. Generate a plot of solution pH versus volume of 0.100 M HCl added for the titration of a solution of 250 mg of CaCO3 in 200.0 mL of water with 0.100 M HCl; assume that the HCl solution is added in 5.00 mL increments. What volume of HCl corresponds to the equivalence point?

7. For a titration of 50.0 mL of 0.288 M $NaOH$, you would like to prepare a 0.200 M HCl solution. The only HCl solution available to you, however, is 12.0 M.

a. How would you prepare 500 mL of a 0.200 M HCl solution?
b. Approximately what volume of your 0.200 M HCl solution is needed to neutralize the $NaOH$ solution?
c. After completing the titration, you find that your “0.200 M” HCl solution is actually 0.187 M. What was the exact volume of titrant used in the neutralization?

8. While titrating 50.0 mL of a 0.582 M solution of HCl with a solution labeled “0.500 M KOH,” you overshoot the endpoint. To correct the problem, you add 10.00 mL of the HCl solution to your flask and then carefully continue the titration. The total volume of titrant needed for neutralization is 71.9 mL.

a. What is the actual molarity of your KOH solution?
b. What volume of titrant was needed to neutralize 50.0 mL of the acid?

9. Complete the following table and generate a titration curve showing the pH versus volume of added base for the titration of

50.0 mL of 0.288 M HCl with 0.321 M $NaOH$. Clearly indicate the equivalence point.

Base Added (mL)	10.0	30.0	40.0	45.0	50.0	55.0	65.0	75.0
pH								

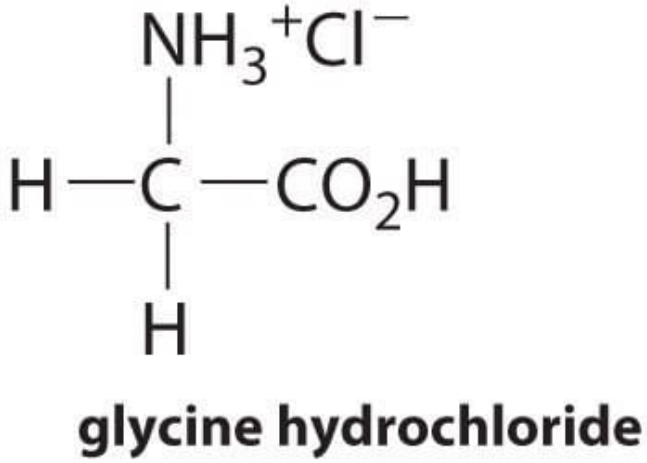
10. The following data were obtained while titrating 25.0 mL of 0.156 M $NaOH$ with a solution labeled "0.202 M HCl." Plot the pH versus volume of titrant added. Then determine the equivalence point from your graph and calculate the exact concentration of your HCl solution.

Volume of HCl (mL)	5	10	15	20	25	30	35
pH	11.46	11.29	10.98	4.40	2.99	2.70	2.52

11. Fill in the data for the titration of 50.0 mL of 0.241 M formic acid with 0.0982 M KOH. The pKa of formic acid is 3.75. What is the pH of the solution at the equivalence point?

Volume of Base Added (mL)	0	5	10	15	20	25
pH						

12. Glycine hydrochloride, which contains the fully protonated form of the amino acid glycine, has the following structure:



glycine hydrochloride

It is a strong electrolyte that completely dissociates in water. Titration with base gives two equivalence points: the first corresponds to the deprotonation of the carboxylic acid group and the second to loss of the proton from the ammonium group. The corresponding equilibrium equations are as follows:

$$^{+}NH_3 - CH_2 - CO_2H\,(aq) \rightleftharpoons \quad pK_{a1} = 2.3 \tag{17.E.2}$$

$$^{+}NH_3 - CH_2 - CO_2\,(aq) + H^{+} \tag{17.E.3}$$

$$^{+}NH_3 - CH_2 - CO_2\,(aq) \rightleftharpoons \quad pK_{a2} = 9.6 \tag{17.E.4}$$

$$NH_2 - CH_2 - COO\,(aq) + H^{+} \tag{17.E.5}$$

Given 50.0 mL of solution that is 0.430 M glycine hydrochloride, how many milliliters of 0.150 M KOH are needed to fully deprotonate the carboxylic acid group?

a. How many additional milliliters of KOH are needed to deprotonate the ammonium group?
b. What is the pH of the solution at each equivalence point?
c. How many milliliters of titrant are needed to obtain a solution in which glycine has no net electrical charge? The pH at which a molecule such as glycine has no net charge is its isoelectric point. What is the isoelectric point of glycine?

13. What is the pH of a solution prepared by adding 38.2 mL of 0.197 M HCl to 150.0 mL of 0.242 M pyridine? The pKb of pyridine is 8.77.

14. What is the pH of a solution prepared by adding 40.3 mL of 0.289 M $NaOH$ to 150.0 mL of 0.564 M succinic acid ($HO_2CCH_2CH_2CO_2H$)? (For succinic acid, pKa1 = 4.21 and pKa2 = 5.64).

14. Calculate the pH of a 0.15 M solution of malonic acid ($HO_2CCH_2CO_2H$), whose pKa values are as follows: pKa1 = 2.85 and pKa2 = 5.70.

Answers

1.

a.$pH = -log([H_3O^+]) = -log(1.218) = -0.086$

$[HCl] = [H^+]$

$M_1V_1 = M_2V_2 \rightarrow (6.09\ M)(25\ mL) = (x)(125\ mL) \rightarrow x = 1.218$

b. $pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 0.80 = 13$

$pOH = -log([OH^-]) = -log(0.159) = 0.80$

$[NaOH] = [OH^-]$

$M_1V_1 = M_2V_2 \rightarrow (2.55\ M)(5.0\ mL) = (x)(80\ mL) \rightarrow x = 0.159$

2.

$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 1.321 = 12.7$

$HCl : 50.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{0.225\ mol}{1\ L} = 0.01125\ mol$

$NaOH : 100.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{0.184\ mol}{1\ L} = 0.0184\ mol$

Note the number of moles for $NaOH$ is greater than HCl, therefore we calculate pOH.

$0.0184 - 0.01125 = 0.00715\ mol$

$\frac{0.00715\ mol}{.15\ L} = 0.0477$

$pOH = -log([OH^-]) = -log(0.0477) = 1.321$

3. $M_1V_1 = M_2V_2 \rightarrow (0.50\ M)(x\ L) = (0.86\ M)(0.25\ L) \rightarrow x\ L = 4.3 \times 10^{-2}\ L$

4. Video Solution

a. $pH = pK_a + log(\frac{C_2H_3NaO_2}{C_2H_4O_2}) = 4.76 + log(\frac{0.0935}{0.0105}) = 5.71$

$HCl : 100\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{0.0105\ mol}{1\ L} = 0.0105\ mol$

$C_2H_3NaO_2 : 100\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{0.115\ mol}{1\ L} = 0.0115\ mol$

$C_2H_3NaO_2\ (s) + HCl\ (aq) \rightarrow C_2H_4O_2\ (aq) + NaCl\ (s)$

	$C_2H_3NaO_2$	HCl	$C_2H_4O_2$	$NaCl$

I	0.0115	0.0105	0	-
C	-0.0105	-0.0105	+0.0105	-
E	0.0935	0	0.0105	-

b. $pH = pK_a + log(\frac{C_2H_3NaO_2}{C_2H_4O_2}) = 4.76 + log(\frac{0.01}{0.005}) = 5.05$

$HCl : 100\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{0.0105\ mol}{1\ L} = 0.005\ mol$

$C_2H_3NaO_2 : 100\ mL \times \frac{1\ L}{1{,}000\ mL} \times \frac{0.115\ mol}{1\ L} = 0.015\ mol$

$C_2H_3NaO_2\ (s) + HCl\ (aq) \rightarrow C_2H_4O_2\ (aq) + NaCl\ (s)$

	$C_2H_3NaO_2$	HCl	$C_2H_4O_2$	$NaCl$
I	0.015	0.005	0	0
C	-0.005	-0.005	+0.005	+0.005
E	0.01	0	0.005	0.005

c. $pH = 14 - pOH = 14 - (-log(\frac{0.0118 - 0.0109}{0.2\ L})) = 11.7$

$CH_3COOH : 0.1\ L \times 0.109\ M = 0.0109\ mol$

$NaOH : 0.1\ L \times 0.118\ M = 0.0118\ mol$

$CH_3COOH\ (aq) + NaOH\ (aq) \rightarrow H_2O\ (l) + CH_3COO^-Na\ (aq)$

	CH_3COOH	$NaOH$	H_2O	CH_3COONa
I	0.0109	0.0118	-	0
C	-0.0109	-0.0109	-	+0.0109
E	0	9×10^{-4}	-	0.0109

d. $pH = 4.76 + log(\frac{0.0055}{0.0943}) = 3.53$

$CH_3COOH : 0.1\ L \times 0.998\ M = 0.0998\ mol$

$NaOH: 0.05\ L \times 0.110\ M = 0.0055\ mol$

$CH_3COOH\ (aq) + NaOH\ (aq) \rightarrow H_2O\ (l) + CH_3COONa\ (aq)$

	CH_3COOH	$NaOH$	H_2O	CH_3COONa
I	0.0998	0.0055	-	0
C	-0.0055	-0.0055	-	+0.0055
E	0.0943	0	-	0.0055

5. Video Solution

a. $pH = -log(\frac{0.9728}{0.2\ L}) = 4.86$

$HCl: 100\ mL \times \frac{1\ L}{1{,}000\ L} \times 0.983\ M = 0.983\ mol$

$NaF: 100\ mL \times \frac{1\ L}{1{,}000\ L} \times 0.102\ M = 0.0102\ mol$

$HCl\ (aq) + NaF\ (s) \rightarrow NaCl\ (aq) + HF\ (aq)$

	HCl	NaF	$NaCl$	HF
I	0.983	0.0102	-	0
C	-0.0102	-0.0102	-	-0.0102
E	0.9728	0	-	-0.0102

b. $pH = pK_a + log(\frac{[NaF]}{[HF]}) = 3.14 + log(\frac{0.00515}{0.00575}) = 3.09$

$HCl: 50\ mL \times \frac{1\ L}{1{,}000\ L} \times 0.115\ M = 0.00575\ mol$

$NaF: 100\ mL \times \frac{1\ L}{1{,}000\ L} \times 0.109\ M = 0.0109\ mol$

$HCl\ (aq) + NaF\ (s) \rightarrow NaCl\ (aq) + HF\ (aq)$

	HCl	NaF	$NaCl$	HF
I	0.00575	0.0109	-	0

C	-0.00575	-0.00575	-	+0.00575
E	0	0.00515	-	0.00575

c. $pH = 14 - pOH = 14 - (-log(0.0498 - 0.0106)) = 12.6$

$HF: 100\ mL \times \frac{1\ L}{1{,}000\ L} \times 0.106\ M = 0.0106\ mol$

$NaOH: 50\ mL \times \frac{1\ L}{1{,}000\ L} \times 0.996\ M = 0.0498\ mol$

$HF\ (aq) + NaOH\ (aq) \rightarrow NaF\ (aq) + H_2O\ (aq)$

$HCl(aq) + NaOH(aq) \rightarrow NaCl\ (aq) + H_2O$

d.$pH = pK_a + log(\frac{[C_2H_3NaO_2]}{[CH_3COOH]}) = 4.76 + log(\frac{0.0107}{0.04935}) = 4.10$

$C_2H_3NaO_2: 0.1\ L \times 0.107\ M = 0.0107$

$CH_3COOH: 0.05\ mL \times 0.987\ M = 0.04935$

$CH_3COOH\ (aq) + H_2O \rightarrow C_2H_3O^- + H_3O^+$

6.

$CaCO_3\ (aq) + 2\ HCl\ (aq) \rightarrow CaCl_2\ (aq) + H_2O\ (l) + CO_2\ (g)$

$CO_3^{2-}\ (aq) + H^+\ (aq) \rightleftharpoons HCO_3^-\ (aq)$

$HCO_3^{2-}\ (aq) + H^+\ (aq) \rightleftharpoons H_2CO_3\ (aq)$

$K_{a1} = 4.3 \times 10^{-7}$

$K_{a2} = 5.0 \times 10^{-11}$

At 0 mL addition of HCl: $pH = 14 - pOH = 14 - (-log(\sqrt{0.0125 \times \frac{10^{-14}}{5.0 \times 10^{-11}}}) = 11.20$

$CaCO_3: 250\ mg \times \frac{1\ g}{1{,}000\ mg} \times \frac{1\ mol}{100.0869\ g} \times \frac{1}{200\ mL \times \frac{1\ L}{1{,}000\ mL}} = 0.0125\ M$

At 5 mL addition of HCl: $pH = -log(5 \times 10^{-11}) + log(\frac{0.002}{0.0005}) = 10.9$

$CaCO_3: 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl: 0.005\ L \times 0.1\ M = 0.0005\ mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.0005	0
C	-0.0005	-0.0005	0.0005

E	0.002	0	0.0005

At 10 mL addition of HCl: $pH = -log(5 \times 10^{-11}) + log(\frac{0.001}{0.0015}) = 10.5$

$CaCO_3 : 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl : 0.01\ L \times 0.1\ M = 0.001\ mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.001	0
C	-0.001	-0.001	0.001
E	0.0015	0	0.001

At 15 mL addition of HCl:$pH = -log(5 \times 10^{-11}) + log(\frac{0.001}{0.0015}) = 10.1$

$CaCO_3 : 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl : 0.015\ L \times 0.1\ M = 0.0015\ mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.0015	0
C	-0.0015	-0.0015	0.0015
E	0.001	0	0.0015

At 20 mL addition of HCl:$pH = -log(5 \times 10^{-11}) + log(\frac{5 \times 10^{-4}}{0.002}) = 9.7$

$CaCO_3 : 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl : 0.02\ L \times 0.1\ M = 0.002\ mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.002	0

C	-0.002	-0.002	0.002
E	5×10^{-4}	0	0.002

At 25 mL addition of HCl: first equivalence point: $pH = \frac{-log(K_{a1}) - log(K_{a2})}{2} = \frac{-log(4.3 \times 10^{-7}) - log(5.0 \times 10^{-11})}{2} = 8.33$

$HCO_3^- : 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl : 0.025\ L \times 0.1\ M = 0.0025\ mol$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0025	0
C	-0.0025	-0.0025	0.0025
E	0	0	0.0025

At 30 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.0005}) = 7.07$

$HCO_3^- : 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl : 0.03\ L \times 0.1\ M = 0.003$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.003	0
C	-0.0025	-0.0025	0.0025
E	0	5×10^{-4}	0.0025

At 35 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.001}) = 6.76$

$HCO_3^- : 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl : 0.035\ L \times 0.1\ M = 0.0035$

	HCO_3^-	H^+	H_2CO_3

I	0.0025	0.0035	0
C	-0.0025	-0.0025	0.0025
E	0	0.001	0.0025

At 40 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.003}) = 6.59$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.040\ L \times 0.1\ M = 0.004$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.004	0
C	-0.0025	-0.0025	0.0025
E	0	0.0015	0.0025

At 45 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.002}) = 6.46$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.045\ L \times 0.1\ M = 0.0045$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0045	0
C	-0.0025	-0.0025	0.0025
E	0	0.002	0.0025

At 50 mL addition of HCl: second equivalence point: $pH = 3.86$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.05\ L \times 0.1\ M = 0.005$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.005	0
C	-0.0025	-0.0025	0.0025
E	0	0.0025	0.0025

At 55 mL addition of HCl: $pH = -log(\frac{0.003}{0.055}) = 1.26$

$HCO_3^-: 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl: 0.055\ L \times 0.1\ M = 0.0055$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0055	0
C	-0.0025	-0.0025	0.0025
E	0	0.003	0.0025

At 60 mL addition of HCl: $pH = -log(\frac{0.0035}{0.06}) = 1.23$

$HCO_3^-: 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl: 0.06\ L \times 0.1\ M = 0.006$

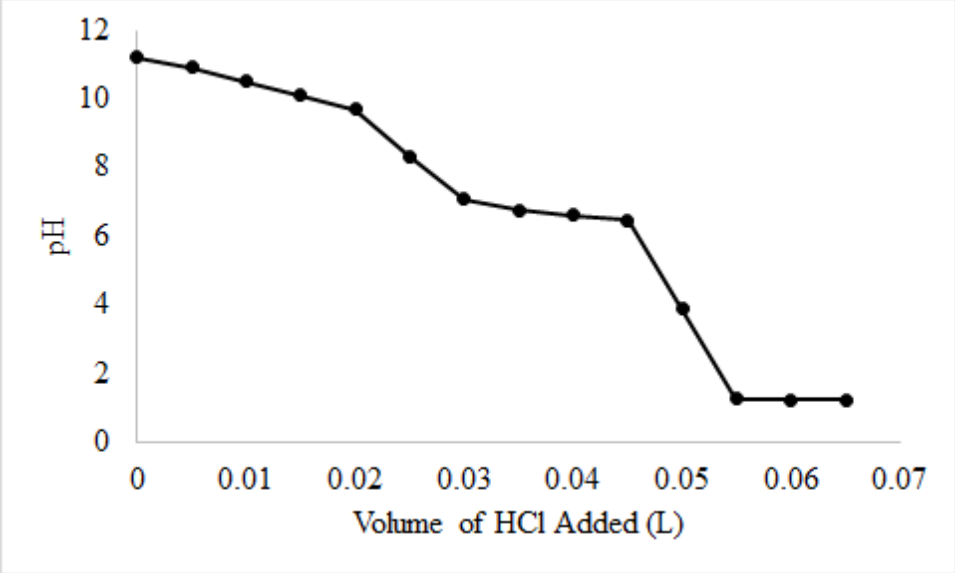
	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.006	0
C	-0.0025	-0.0025	0.0025
E	0	0.0035	0.0025

At 65 mL addition of HCl: $pH = -log(\frac{0.0040}{0.065}) = 1.21$

$HCO_3^-: 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl: 0.06\ L \times 0.1\ M = 0.006$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0065	0
C	-0.0025	-0.0025	0.0025
E	0	0.0040	0.0025



7. Video Solution

a. $M_1V_1 = M_2V_2 \rightarrow V_2 = \frac{M_1V_1}{V_2} = \frac{(0.2\ M)(0.5\ L)}{12.0\ M} = 8.33 \times 10^{-3}\ L$ Therefore, dilute 8.33 mL of 12.0 M HCl to 500.0 mL.

b. $M_1V_1 = M_2V_2 \rightarrow V_2 = \frac{M_1V_1}{V_2} = \frac{(0.288\ M)(0.05\ L)}{0.2\ M} = 7.20 \times 10^{-3}\ L$

c. $M_1V_1 = M_2V_2 \rightarrow V_2 = \frac{M_1V_1}{V_2} = \frac{(0.288\ M)(0.05\ L)}{0.187\ M} = 7.70 \times 10^{-2}$

8.

a. $M_1V_1 = M_2V_2 \rightarrow M_2 = \frac{M_1V_1}{V_2} = \frac{(0.582\ M)(0.060\ L)}{0.0719\ L} = 0.49\ M$

b. $M_1V_1 = M_2V_2 \rightarrow V_2 = \frac{M_1V_1}{M_2} = \frac{(0.582\ M)(0.050\ L)}{0.49\ M} = 59.4 \times 10^{-2}\ L$

9.

Volume of Base Added (mL)	10.0	30.0	40.0	45.0	50.0	55.0	65.0	75.0
pH	0.73	1.22	1.76	7	12.2	12.5	13.0	13.1

$NaOH\ (aq) + HCl\ (aq) \rightarrow NaCl\ (s) + H_2O\ (l)$

At 0 mL of base added: $pH = -log(0.288) = 0.54$

At 10 mL of base added: $pH = -log(\frac{0.0144-0.00321}{0.06}) = 0.73$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.01\ L \times 0.321\ M = 0.00321$

At 30 mL of base added: $pH = -log(\frac{0.0144-0.00963}{0.08}) = 1.22$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.03\ L \times 0.321\ M = 0.00963$

At 40.0 mL of base added: $pH = -log(\frac{0.0144-0.01284}{0.09}) = 1.76$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.04\ L \times 0.321\ M = 0.01284$

At 45.0 mL of base added: $pH = 7$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.045\ L \times 0.321\ M = 0.0144$

All HCl will neutralize at the equivalence point $[H^+] = [OH^-]$ and the pH of the solution is 7.

At 50.0 mL base added: $pH = 14 - pOH = 14 - log(\frac{0.01605-0.0144}{0.1}) = 12.2$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.050\ L \times 0.321\ M = 0.01605$

At 55 mL base added: $pH = 14 - pOH = 14 - log(\frac{0.01605-0.0144}{0.1}) = 12.5$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.055\ L \times 0.321\ M = 0.017655$

At 65 mL base added: $pH = 14 - pOH = 14 - log(\frac{0.020865-0.0144}{0.07}) = 13.0$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.065\ L \times 0.321\ M = 0.020865$

At 75 mL base added: $pH = 14 - pOH = 14 - log(\frac{0.024075-0.0144}{0.08}) = 13.1$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.075\ L \times 0.321\ M = 0.024075$

10.

The equivalence point is at pH 7 and this occurs at 0.0193 L.

$V_2 = \frac{(0.156\ M)(0.025\ L)}{0.202} = 0.0193\ L$

11.

pH at equivalence point: $14 - (-log\sqrt{(\frac{10^{-14}}{10^{-3.75}} \times \frac{0.01205}{0.05+0.1227})}) = 8.30$

$0.05\ L \times 0.241\ M = 0.01205\ mol$

$V_2 = \frac{(0.05\ L)(0.241\ M)}{0.0982} = 0.1227\ L$

Volume of Base Added (mL)	0	5	10	15	20	25
pH	2.18	2.38	2.70	2.89	3.04	3.16

At 0 mL of base added: $pH = -log([H^+]) = -log(2.52 \times 10^{-6}) = 2.18$

$[H^+] = \sqrt{10^{-3.75} \times 0.241\ M} = 2.52 \times 10^{-6}$

At 5 mL of base added: $pH = 3.75 + log(\frac{4.91 \times 10^{-4}}{0.01205 - 4.91 \times 10^{-4}}) = 2.38$

$KOH: 0.05\ L \times 0.0982\ M = 4.91 \times 10^{-4}\ mol$

$CH_2O_2: 0.05\ L \times 0.241\ M = 0.01205\ mol$

At 10 mL of base added: $pH = 3.75 + log(\frac{9.82 \times 10^{-4}}{0.01205 - 9.82 \times 10^{-4}}) = 2.70$

$KOH: 0.01\ L \times 0.0982\ M = 9.82 \times 10^{-4}\ mol$

$CH_2O_2: 0.05\ L \times 0.241\ M = 0.01205\ mol$

At 15 mL of base added:$pH = 3.75 + log(\frac{0.001473}{0.01205 - 0.001473} = 2.89$

$KOH: 0.015\ L \times 0.0982\ M = 0.001473$

$CH_2O_2: 0.05\ L \times 0.241\ M = 0.01205$

At 20 mL of base added: $pH = 3.75 + log(\frac{0.001964}{0.01205 - 0.001964}) = 3.04$

$KOH: 0.02\ L \times 0.0982\ M = 0.001964$

$CH_2O_2: 0.05\ L \times 0.241\ M = 0.01205$

At 25 mL base added: $pH = 3.75 + log(\frac{0.002455}{0.01205 - 0.002455}) = 3.16$

$KOH: 0.025\ L \times 0.0982\ M = 0.002455\ mol$

$CH_2O_2: 0.05\ L \times 0.241\ M = 0.01205$

12. $M_1V_1 = M_2V_2 \rightarrow V_2 = \frac{M_1V1}{M_2} = \frac{(0.430\ M)(0.05\ L)}{0.150\ M} = 1.42 \times 10^{-1}\ L$

143 mL are needed to fully deprotonate the carboxylic acid group.

a. 143 additional milliliters of KOH are needed to deprotonate the ammonium group.

b. At the first equivalence point: $pH = \frac{(pKa_1 + pKa_2)}{2} = 5.95$

c. 143 mL of titrant are needed to obtain a solution in which glycine has no electrical charge. The isoelectric point of glycine 5.95.

13.

$pH = pK_a + log(\frac{[C_5H_5N]}{[C_5H_5NH^+]}) = (14 - 8.77) + log(\frac{0.02996}{0.0063434}) = 5.90$

$C_5H_5N\ (aq) + HCl\ (aq) \rightarrow C_5H_5NH^+\ (aq) + Cl^-\ (aq)$

$HCl: 32.2\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.197\ M = 0.0063434\ mol$

$C_5H_5N: 150\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.242\ M = 0.0363\ mol$

	C_5H_5N	HCl	$C_5H_5NH^+$	Cl^-
I	0.0363	0.0063434	0	-
C	-0.0063434	-0.0063434	+0.0063434	-
E	0.02996	0	0.0063434	-

14. $pH = \frac{(4.21+5.64)}{2} = 4.93$

15. $pH = \frac{(2.85+5.70)}{2} = 4.25$

17.4: Solubility Equilibria

Conceptual Problems

1. Write an expression for K_{sp} for each salt.

a. AgI
b. CaF_2
c. $PbCl_2$
d. Ag_2CrO_4

2. Some species are not represented in a solubility product expression. Why?

3. Describe the differences between Q and K_{sp}.

4. How can an ion product be used to determine whether a solution is saturated?

5. When using K_{sp} to directly compare the solubilities of compounds, why is it important to compare only the K_{sp} values of salts that have the same stoichiometry?

6. Describe the effect of a common ion on the solubility of a salt. Is this effect similar to the common ion effect found in buffers? Explain your answer.

7. Explain why the presence of $MgCl_2$ decreases the molar solubility of the sparingly soluble salt $MgCO_3$.

Conceptual Answers

1.

a. $K_{sp} = [Ag^+][I^-]$

b. $K_{sp} = [Ca^{2+}][F^-]^2$

c. $K_{sp} = [Pb^{2+}][Cl^-]^2$

d. $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

2. The solubility constant expression, K_{sp} is an equilibrium constant for a solid substance dissolving in a an aqueous solution. Thus, it is a measure of solubility and species that do not dissolve are not represented in the solubility product expression.

3. The main difference between Q and K_sp is that Q describes a reaction that is not at equilibrium unlike K_{sp}.

4. An ion product can be used to determine whether a solution is saturated as it is compared to K_{sp} where there are three possible conditions for an aqueous solution of an ionic solid:

    1. \(Q
    2. $Q = K_{sp}$. The solution is saturated and at equilibrium.
    3. $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

5. For a 1:1 salt, the molar solubility is simply $\sqrt{K_{\text{sp}}}$; for a 2:1 salt, the molar solubility is $\sqrt[3]{K_{\text{sp}}/4}$. Consequently, the magnitudes of K_{sp} can be correlated with molar solubility only if the salts have the same stoichiometry.
6. By the presence of a common ion, the solubility of any sparingly soluble salt is always decreased. This is similar to the common ion effect found in buffers as adding a common cation or anion shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle.

7. Because of the common ion effect. Adding a soluble Mg^{2+} salt increases [Mg2+] in solution, and Le Chatelier's principle predicts that this will shift the solubility equilibrium of $MgCO_3$ to the left, decreasing its solubility.

Numerical Problems

1. Predict the molar solubility of each compound using the K_{sp} values given in Chapter 26.

    a. $Cd(IO_3)_2$
    b. $AgCN$
    c. HgI_2

2. Predict the molar solubility of each compound using the K_{sp} values given.

    a. Li_3PO_4: 2.37×10^{-11}
    b. $Ca(IO_3)_2$: 6.47×10^{-6}
    c. $Y(IO_3)_3$: 1.12×10^{-10}

3. A student prepared 750 mL of a saturated solution of silver sulfate (Ag_2SO_4). How many grams of Ag_2SO_4 does the solution contain? $K_{\text{sp}} = 1.20 \times 10^{-5}$.

4. Given the K_{sp} values in Table 17.1 "Solubility Products for Selected Ionic Substances at 25°C" and Appendix B, predict the molar concentration of each species in a saturated aqueous solution.

    a. silver bromide
    b. lead oxalate
    c. iron(II) carbonate
    d. silver phosphate
    e. copper(I) cyanide

5. Given the K_{sp} values in Table 17.1 "Solubility Products for Selected Ionic Substances at 25°C" and Appendix B predict the molar concentration of each species in a saturated aqueous solution.

    a. copper(I) chloride
    b. lanthanum(III) iodate
    c. magnesium phosphate

d. silver chromate
e. strontium sulfate

6. Silicon dioxide, the most common binary compound of silicon and oxygen, constitutes approximately 60% of Earth's crust. Under certain conditions, this compound can react with water to form silicic acid, which can be written as either H_4SiO_4 or $Si(OH)_4$. Write a balanced chemical equation for the dissolution of SiO_2 in basic solution. Write an equilibrium constant expression for the reaction.

7. The $K_{sp}$of $Mg(OH)_2$ is 5.61×10^{-12}. If you tried to dissolve 24.0 mg of $Mg(OH)_2$ in 250 mL of water and then filtered the solution and dried the remaining solid, what would you predict to be the mass of the undissolved solid? You discover that only 1.0 mg remains undissolved. Explain the difference between your expected value and the actual value.

8. The Ksp of lithium carbonate is 8.15×10^{-4}. If 2.34 g of the salt is stirred with 500 mL of water and any undissolved solid is filtered from the solution and dried, what do you predict to be the mass of the solid? You discover that all of your sample dissolves. Explain the difference between your predicted value and the actual value.

9. You have calculated that 24.6 mg of $BaSO_4$ will dissolve in 1.0 L of water at 25°C. After adding your calculated amount to 1.0 L of water and stirring for several hours, you notice that the solution contains undissolved solid. After carefully filtering the solution and drying the solid, you find that 22.1 mg did not dissolve. According to your measurements, what is the K_{sp} of barium sulfate?

10. In a saturated silver chromate solution, the molar solubility of chromate is 6.54×10^{-5}. What is the K_{sp}?

11. A saturated lead(II) chloride solution has a chloride concentration of 1.62×10^{-2} mol/L. What is the K_{sp}?

12. From the solubility data given, calculate K_{sp} for each compound.

    a. AgI: 2.89×10^{-7} g/100 mL
    b. SrF_2: 1.22×10^{-2} g/100 mL
    c. $Pb(OH)_2$: 78 mg/500 mL
    d. $BiAsO_4$: 14.4 mg/2.0 L

13. From the solubility data given, calculate K_{sp} for each compound.

    a. $BaCO_3$: 10.0 mg/500 mL
    b. CaF_2: 3.50 mg/200 mL
    c. $Mn(OH)_2$: 6.30×10^{-4} g/300 mL
    d. Ag_2S: 1.60×10^{-13} mg/100 mL

14. Given the following solubilities, calculate Ksp for each compound.

    a. $BaCO_3$: 7.00×10^{-5} mol/L
    b. CaF_2: 1.70 mg/100 mL
    c. $Pb(IO_3)_2$: 2.30 mg/100 mL
    d. SrC_2O_4: 1.58×10^{-7}mol/L

15. Given the following solubilities, calculate K_{sp} for each compound.

    a. Ag_2SO_4: 4.2×10^{-1} g/100 mL
    b. $SrSO_4$: 1.5×10^{-3} g/100 mL
    c. CdC_2O_4: 6.0×10^{-3} g/100 mL
    d. $Ba(IO_3)_2$: 3.96×10^{-2} g/100 mL

16. The K_{sp} of the phosphate fertilizer $CaHPO_4 \cdot 2H_2O$ is 2.7×10^{-7} at 25°C. What is the molar concentration of a saturated

solution? What mass of this compound will dissolve in 3.0 L of water at this temperature?

17. The K_{sp} of zinc carbonate monohydrate is 5.5×10^{-11} at 25°C. What is the molar concentration of a saturated solution? What mass of this compound will dissolve in 2.0 L of water at this temperature?

18. Silver nitrate eye drops were formerly administered to newborn infants to guard against eye infections contracted during birth. Although silver nitrate is highly water soluble, silver sulfate has a K_{sp} of 1.20×10^{-5} at 25°C. If you add 25.0 mL of 0.015 M $AgNO_3$to 150 mL of 2.8×10^{-3} M Na_2SO_4, will you get a precipitate? If so, what will its mass be?

19. Use the data in Appendix B to predict whether precipitation will occur when each pair of solutions is mixed.

    a. 150 mL of 0.142 M $Ba(NO_3)_2$ with 200 mL of 0.089 M NaF
    b. 250 mL of 0.079 M K_2CrO_4 with 175 mL of 0.087 M $CaCl_2$
    c. 300 mL of 0.109 M $MgCl_2$ with 230 mL of 0.073 M $Na_2(C_2O_4)$

20. What is the maximum volume of 0.048 M $Pb(NO_3)_2$ that can be added to 250 mL of 0.10 M NaSCN before precipitation occurs?K_{sp} = 2.0×10^{-5} for $Pb(SCN)_2$.

21. Given 300 mL of a solution that is 0.056 M in lithium nitrate, what mass of solid sodium carbonate can be added before precipitation occurs (assuming that the volume of solution does not change after adding the solid)? K_{sp} = 8.15×10^{-4} for Li_2CO_3.

22. Given the information in the following table, calculate the molar solubility of each sparingly soluble salt in 0.95 M $MgCl_2$.

Saturated Solution	K_{sp}
$MgCO_3 \cdot 3H_2O$	2.4×10^{-6}
$Mg(OH)_2$	5.6×10^{-12}
$Mg_3(PO_4)_2$	1.04×10^{-24}

Numerical Answers

1.

a. $K_{sp} = [Cd^{2+}][IO_3]^2 \rightarrow 2.5 \times 10^{-8} = x(2x)^2 \rightarrow 2.5 \times 10^{-8} = 4x^3 \rightarrow x = 1.84 \times 10^{-3}$

b. $K_{sp} = [Ag^{+}][CN^{-}] \rightarrow 1.6 \times 10^{-14} = (x)(x) \rightarrow x = 7.73 \times 10^{-9}$

c. $K_{sp} = [Hg^{2+}][I^{-}]^2 \rightarrow 2.9 \times 10^{-29} = (x)(2x)^2 \rightarrow 1.94 \times 10^{-10}$

2.

a. $K_{sp} = [Li^{+}]^3[PO_4^{3-}] \rightarrow 2.37 \times 10^{-11} = (3x)^3(x) \rightarrow x = 9.68 \times 10^{-4}$

b. $K_{sp} = [Ca^{2+}][IO_3^{-}]^2 \rightarrow 6.47 \times 10^{-6} = (x)(2x)^2 \rightarrow 1.17 \times 10^{-2}$

c. $K_{sp} = [Y^{3+}][IO_3]^{-}]^3 \rightarrow 1.12 \times 10^{-10} = (x)(3x)^3 \rightarrow x = 1.42 \times 10^{-3}$

3. $0.750\ L \times \frac{0.0144\ mol}{1\ L} \times \frac{311.199\ g}{1\ mol} = 3.37\ g$

$K_{sp} = [Ag^{+}]^2[SO_4^{2-}] \rightarrow 1.20 \times 10^{-5} = (2x)^2(x) \rightarrow x = 0.0144$

4.

a. $K_{sp} = [Ag^{+}][Br^{-}] \rightarrow 5.35 \times 10^{-13} = (x)(x) \rightarrow x = 7.31 \times 10^{-7}$

b. $K_{sp} = [PB^{2+}][C_2O_4] \rightarrow 8.5 \times 10^{-9} = (x)(x) \rightarrow x = 9.2 \times 10^{-5}$

c. $K_{sp} = [Fe^{2+}][CO_3^{2-}] \rightarrow 3.13 \times 10^{-11} = (x)(x) \rightarrow x = 5.60 \times 10^{-6}$

d. $K_{sp} = [Ag^{+}]^3[PO_4^{3-}] \rightarrow 8.89 \times 10^{-17} = (3x)^3(x) \rightarrow x = 4.26 \times 10^{-5}$

e. $K_{sp} = [Cu][CN] \rightarrow 3.47 \times 10^{-20} = (x)(x) \rightarrow x = 1.86 \times 10^{-10}$

5.

a. $K_{sp} = [Cu][CN] \rightarrow 1.72 \times 10^{-20} = (x)(x) \rightarrow x = 4.15 \times 10^{-4}$

b. $K_{sp} = [La^{3+}][IO_3^{-}]^3] \rightarrow 7.50 \times 10^{-12} = (x)(3x)^3 \rightarrow x = 7.26 \times 10^{-4}$

c. $K_{sp} = [Mg^{2+}]^3[PO_4^{3-}]^2 \rightarrow 1.04 \times 10^{-24} = (3x)^3(2x)^2 \rightarrow x = 6.26 \times 10^{-6}$

d. $K_{sp} = [Ag^{+}]^2[CrO_4^{2-}] \rightarrow 1.12 \times 10^{-12} = (2x)^2(x) \rightarrow 6.54 \times 10^{-5}$

e. $K_{sp} = [Sr^{2+}][SO_4^{2-}] \rightarrow 3.44 \times 10^{-7} = (x)(x) \rightarrow x = 5.87 \times 10^{-4}$

6.

$SiO_2\ (g) + H_2O\ (l) \rightarrow Si(OH)_4\ (aq)$

$K_{sp} = [Si^{4+}][OH^{-}]^4$

7. 22.4 mg; a secondary reaction occurs, where OH^- from the dissociation of the salt reacts with H^+ from the dissociation of water. This reaction causes further dissociation of the salt (Le Chatelier's principle).

$K_{sp} = [Mg^{2+}][OH^{-}]^2 \rightarrow 5.61 \times 10^{-12} = (x)(2x)^2 \rightarrow x = 1.12 \times 10^{-4}$

8.

$Predicted\ mass: \frac{5.88 \times 10^{-2}\ mol}{1\ L} \times \frac{73.891\ g}{1\ mol} \times 0.5\ L = 2.17\ g$

$K_{sp} = [Li^{+}]^2[CO_3^{2-}] \rightarrow 8.15 \times 10^{-4} = (2x)^2(x) \rightarrow x = 5.88 \times 10^{-2}$

The difference between the predicted value and the actual value occurs because the carbonate from the dissociation of the salt reacts with the H^+ from the dissociation of water. This reaction causes further dissociation of the salt (Le Chatelier's principle).

9.

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (x)(x) = x^2 = (1.07 \times 10^{-5}\ M)^2 = 1.15 \times 10^{-10}$

$BaSO_4: (24.6 - 22.1\ mg) \times \frac{1\ g}{1{,}000\ mg} \times \frac{1\ mol}{233.38\ g} \times \frac{1}{1.0\ L} = 1.07 \times 10^{-5}\ M$

10. $K_{sp} = [Ag^{+}]^2[CrO_4^{2-}] = (2x)^2(x) = 4x^3 = 4(6.54 \times 10^{-5}) = 1.12 \times 106{-}12$

11. $K_{sp} = [Pb^{2+}][Cl^{-}]^2 = (x)(2x)^2 = 4x^3 = 4(3.24 \times 10^{-2})^3 = 1.70 \times 10^{-5}$

12.

a. $K_{sp} = [Ag^{+}][I^{-}] = x^2 = (1.23 \times 10^{-8})^2) = 1.52 \times 10^{-16}$

$AgI: (2.89 \times 10^{-7}\ g \times \frac{1\ mol}{234.77\ g} \times \frac{1}{0.1\ L} = 1.23 \times 10^{-8}$

b. $K_{sp} = [Sr^{2+}][F^{-}]^2] = (x)(2x)^2 = 4x^3 = 4(9.72 \times 10^{-4})^3 = 3.66 \times 10^{-9}$

$SrF_2 = 1.22 \times 10^{-2}\ g \times \frac{1\ mol}{125.62\ g} \times \frac{1}{0.1\ L} = 9.72 \times 10^{-4}$

c. $K_{sp} = [Pb^{2+}][OH^{-}]^2 = 4x^3 = 4(6.47 \times 10^{-4})^3 = 1.08 \times 10^{-9}$

$Pb(OH)_2 = 0.078\ g \times \frac{1\ mol}{241.21\ g} \times \frac{1}{0.1\ L} = 6.47 \times 10^{-4}$

d. $K_{sp} = [Bi^{3+}][AsO_4^{3-}] = x^2 = (2.05 \times 10^{-5})^2 = 4.21 \times 10^{-10}$

$BiAsO_4 = 0.0144\ g \times \frac{1\ mol}{350.924\ g} \times \frac{1}{2\ L} = 2.05 \times 10^{-5}$

13.

a. $K_{sp} = [Ba^{2+}][CO_3^{2-}] = x^2 = (1.01 \times 10^{-4})^2 = 1.03 \times 10^{-8}$

$BaCO_3 : 0.01\ g \times \frac{1\ mol}{197.34\ g} \times \frac{1}{0.5\ L} = 1.01 \times 10^{-4}$

b. $K_{sp} = [Ca^{2+}][F^-]^2 = 4x^3 = 4(2.24 \times 10^{-4})^3 = 4.51 \times 10^{-11}$

$CaF_2 : 0.0035\ g \times \frac{1\ mol}{78.07\ g} \times \frac{1}{0.2\ L} = 2.24 \times 10^{-4}$

c. $K_{sp} = [Mn^{2+}][OH^-]^2 = 4x^3 = 4(2.36 \times 10^{-5})^3 = 5.26 \times 10^{-14}$

$Mn(OH)_2 : 6.30 \times 10^{-4}\ g \times \frac{1\ mol}{88.95\ g} \times \frac{1}{0.3\ L} = 2.36 \times 10^{-5}$

d. $K_{sp} = [Ag^+]^2[S^{2-}] = 4x^3 = 4(6.46 \times 10^{-18})^3 = 1.08 \times 10^{-51}$

$Ag_2S : 1.60 \times 10^{-16}\ g \times \frac{1\ mol}{247.8\ g} \times \frac{1}{0.1\ L} = 6.46 \times 10^{-18}$

14.

a. $K_{sp} = [Ba^{2+}][CO_3^{2-}] = x^2 = (7.0 \times 10^{-5})^2 = 4.90 \times 10^{-9}$

b. $K_{sp} = [Ca^{2+}][F^-]^2 = 4x^3 = 4(2.18 \times 10^{-4})^3 = 4.13 \times 10^{-11}$

$CaF_2 : 0.0017\ g \times \frac{1\ mol}{78.07\ g} \times \frac{1}{0.1\ L} = 2.18 \times 10^{-4}$

c. $K_{sp} = [Pb^{2+}][IO_3^-]^2 = 4x^3 = 4(4.13 \times 10^{-5})^3 = 2.82 \times 10^{-13}$

$Pb(IO_3)_2 : 0.0023\ g \times \frac{1\ mol}{557.0053\ g} \times \frac{1}{0.1\ L} = 4.13 \times 10^{-5}$

d. $K_{sp} = [Sr^{2+}][C_2O_4^{2-}] = x^2 = (1.58 \times 10^{-7})^2 = 2.50 \times 10^{-14}$

15.

a. $K_{sp} = [Ag^+]^2[SO_4]^{2-} = 4x^3 = 4(1.35 \times 10^{-2})^3 = 9.8 \times 10^{-6}$

$Ag_2SO_4 : 4.2 \times 10^{-1}\ g \times \frac{1\ mol}{311.799\ g} \times \frac{1}{0.1\ L} = 1.35 \times 10^{-2}$

b. $K_{sp} = [Sr^{2+}][SO_4^{2-}] = x^2 = (8.17 \times 10^{-5})^2 = 6.7 \times 10^{-9}$

$SrSO_4 : 1.5 \times 10^{-3}\ g \times \frac{1\ mol}{183.68\ g} \times \frac{1}{0.1\ L} = 8.17 \times 10^{-5}$

c. $K_{sp} = [Cd^{2+}][C_2O_4^{2-}] = x^2 = (2.99 \times 10^{-4})^2 = 8.9 \times 10^{-8}$

$CdC_2O_4 : 6.0 \times 10^{-3}\ g \times \frac{1\ mol}{200.43\ g} \times \frac{1}{0.1\ L} = 2.99 \times 10^{-4}$

d. $K_{sp} = [Ba^{2+}][IO_3^-]^2 = 4x^3 = 4(8.13 \times 10^{-4})^3 = 2.15 \times 10^{-9}$

$Ba(IO_3)_2 : 3.96 \times 10^{-2}\ g \times \frac{1\ mol}{487.15\ g} \times \frac{1}{0.1\ L} = 8.13 \times 10^{-4}$

16.

$K_{sp} = [Ca^{2+}][HPO_4^{2-}] \rightarrow 2.7 \times 10^{-7} = x^2 \rightarrow x = 5.2 \times 10^{-4}$

$CaHPO4 \cdot 2H2O : 3.0\ L \times \frac{2.7\times10^{-7}\ mol}{1\ L} \times \frac{290.1299\ g}{1\ mol} = 2.35 \times 10^{-4}\ g$

17.

$K_{sp} = [Zn^{2+}][CO_3^{2+}] \rightarrow 5.5 \times 10^{-11} = x^2 \rightarrow x = 7.4 \times 10^{-6}$

2.1 mg

18. $Q = [Ag^+]^2[SO_4^{2-}] = (2.14 \times 10^{-3})^2 \times 2.4 \times 10^{-3} = 1.1 \times 10^{-8} < 1.20 \times 10^{-5}$ Therefore, no precipitate will form.

$Ag^+ : \frac{(0.025\ L)(0.015\ M)}{0.175\ L} = 2.14 \times 10^{-3}$

$SO_4^{2-} : \frac{(0.15\ L)(2.8\times10^{-3}}{0.175\ L} = 2.4 \times 10^{-3}$

19.

a. $Q = [Ba^{2+}][F^-]^2 = (0.060857)(0.05643)^2 = 1.94 \times 10^{-4} > 1.84 \times 10^{-7}$ Therefore, precipitate will form.

$Ba^{2+} : \frac{(0.150)(0.142)}{0.35} = 0.060857$

$F^- : \frac{(0.25)(0.079)}{0.35} = 0.05643$

b. \(Q=[K^{+}][Cl^{-}]=(0.0465)(0.0358)=1.66 \times 10^{-3}<21.7. Therefore, precipitate will not form.

$K^+ : \frac{(0.25)(0.079)}{0.425} = 0.0465$

$Cl^- : \frac{(0.175)(0.087)}{0.425} = 0.0358$

c. $Q = [Mg^{2+}][C_2O_4^{2-}] = (0.0617)(0.0317) = 1.95 \times 10^{-3} > 8.5 \times 10^{-5}$ Therefore, precipitate will form.

$Mg^{2+} : \frac{(0.3)(0.109)}{0.53} = 0.0617$

$C_2O_4 : \frac{(0.23)(0.073)}{0.53} = 0.0317$

20. 520 mL

21. 8.27 g

22.

a. $K_{sp} = \sqrt{2.4 \times 10^{-6}} = 1.55 \times 10^{-3}$

b. $K_{sp} = (\frac{5.6\times10^{-12}}{4})^{\frac{1}{3}} = 1.12 \times 10^{-4}$

c. $K_{sp} = (\frac{1.04\times10^{-24}}{108})^{\frac{1}{5}} = 6.26 \times 10^{-6}$

17.5: Factors that Affect Solubility

Conceptual Problems

1. Do you expect the actual molar solubility of $LaPO_4$ to be greater than, the same as, or less than the value calculated from its K_{sp}? Explain your reasoning.
2. Do you expect the difference between the calculated molar solubility and the actual molar solubility of $Ca_3(PO_4)_2$ to be greater than or less than the difference in the solubilities of $Mg_3(PO_4)_2$? Why?
3. Write chemical equations to describe the interactions in a solution that contains $Mg(OH)_2$, which forms ion pairs, and in one that contains propanoic acid ($CH_3CH_2CO_2H$), which forms a hydrated neutral molecule.
4. Draw representations of $Ca(IO_3)_2$ in solution

a. as an ionic solid.
b. in the form of ion pairs.
c. as discrete ions.

Conceptual Answers

1. It is expected that the molar solubility of \LaPO_{4}\) be less than the value from its K_{sp} because the $K_{sp} = [La^{3+}][PO_4^{3-}] = x^2$ in which the molar solubility would be the square root of of K_{sp}.

2. It would be expected that there would be no difference in the calculated molar solubility and actual molar solubility of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ follow the similar equation: $K_{sp} = 108x^5$. It would ultimately depend on the K_{sp} values as \(x=(\frac{K_{sp}}{108})^{\frac{1}{5}} in which the larger \(K_{sp} gives the larger molar solubility.

3.

$Mg(OH)_2\ (s) \rightleftharpoons Mg^{2+}\ (aq) + 2\ OH^-\ (aq)$

$CH_3CH_2CO_2H\ (aq) \rightleftharpoons CH_3CH_2CO_2^-\ (aq) + H^+\ (aq)$

Numerical Problem

1. Ferric phosphate has a molar solubility of 5.44 × 10^{-16} in 1.82 M Na_3PO_4. Predict its K_{sp}. The actual K_{sp} is 1.3 × 10^{-22}. Explain this discrepancy.

Numerical Answer

1. 9.90 × 10^{-16}; the solubility is much higher than predicted by K_{sp} due to the formation of ion pairs (and/or phosphate complexes) in the sodium phosphate solution.

17.6: Precipitation and Separation of Ions

Questions

1. Iron(II) hydroxide is only sparingly soluble in water at 25°C; its K_{sp} is 7.9×10^{-16}. Calculate the solubility of iron(II) hydroxide in a buffer solution with pH = 7.00.
2. A solution contains 0.60 M Ba^{2+} and 0.30 M Ca^{2+}; K_{sp} values for $BaCrO_4$ and $CaCrO_4$ are 1.2×10^{-10} and 7.1×10^{-4} respectively. What value of $[CrO_4{}^{2-}]$ will result in a maximum separation of these two ions?
3. A solution contains 0.60 M Ba^{2+} and 0.30 M Ca^{2+}; K_{sp} values for $BaCrO_4$ and $CaCrO_4$ are 1.2×10^{-10} and 7.1×10^{-4} respectively. Calculate the $[Ca^{2+}]/[Ba^{2+}]$ ratio in the solution when $[CrO_4{}^{2-}]$ is maintained at $1.2 \times 10^{-3}\ M$.

Solutions

1. ***Answer*** $[Fe^{2+}] = 0.079\ M$
   Consider...
   $[OH^-] = 10^{(-14+7)} = 1.00e\text{-}7\ (buffer)$.
   $[Fe^{2+}](1.00e\text{-}7)^2 = K_{sp}$; $[Fe^{2+}] = ?$
   This Fe^{2+} concentration is low; it is not very soluble in a neutral solution (pH = 7).
   What is $[Fe^{2+}]$ in a solution whose pH = 6.00?
2. ***Answer*** $[CrO_4{}^{2-}] = 2.37e\text{-}3\ M$
   Consider...
   Solid $BaCrO_4$ will form first as $[CrO_4{}^{2-}]$ increases. The maximum $[CrO_4{}^{2-}]$ to precipitate $CaCrO_4$ is estimated as follows.
   $[CrO_4{}^{2-}] = \dfrac{7.1e\text{-}4}{0.30} = 2.37e\text{-}3\ M$
   Estimate $[Ba^{2+}]$ when $[CrO_4{}^{2-}] = 2.3e\text{-}3\ M$, slightly below the maximum concentration.

3. ***Answer*** $\frac{[Ca^2+]}{[Ba^2+]} = 3e6$

   Consider...

   $[\mathrm{Ba}^{2+}] = \frac{1.2e\text{-}10}{1.2e\text{-}3} = 1e\text{-}7;$

   $\frac{[Ca^2+]}{[Ba^2+]} = \frac{0.3}{1e\text{-}7} =$? The ratio of three million is large!

17.7: Qualitative Analysis for Metallic Elements

Conceptual Problem

1. Given a solution that contains a mixture of $NaCl$, $CuCl_2$, and $ZnCl_2$, propose a method for separating the metal ions.

Conceptual Solution

1. Given a solution that contains a mixture of $NaCl$, $CuCl_2$, and $ZnCl_2$, we can first use H_2S to separate the Zn^{2+} through filtration, then use ZnS to separate the Cu^{2+} through filtration, and be left with Na^{+}.

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17.S: Additional Aspects of Aqueous Equilibria (Summary)

17.1: The Common-Ion Effect

The common-ion effect argues that the dissociation of a weak electrolyte is decreased by adding a strong electrolyte to the solution that has a **common ion** with the weak electrolyte.

17.2: Buffered Solutions

Buffers are solutions that resist a change in pH

17.2.1 Composition and Action of Buffered Solutions

- buffers have both acidic and basic species to neutralize H^+ and OH^- ions
- acid dissociation equilibrium in buffered solution

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$$

with

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

or

$$[H^+] = K_a \frac{[HX]}{[X^-]}$$

  - pH determined by: value of K_a and the ratio of $[HX]/[X^-]$
  - if OH^- added:
    - $$OH^-(aq) + HX(aq) \rightleftharpoons H_2O(l) + X^-(aq)$$
      - Therefore [HX] decreases and $[X^-]$ increases
      - if amounts of HX and X^- present are very much larger than the amount of OH^- added, then the ratio of $[HX]/[X^-]$ will not change much, and so the increase in pH due to the added hydroxide ion is rather small
  - when [HX] and $[X^-]$ are about the same, buffers are most effective: i.e., when $[H^+] = K_a$

17.2.2 Buffer Capacity and pH

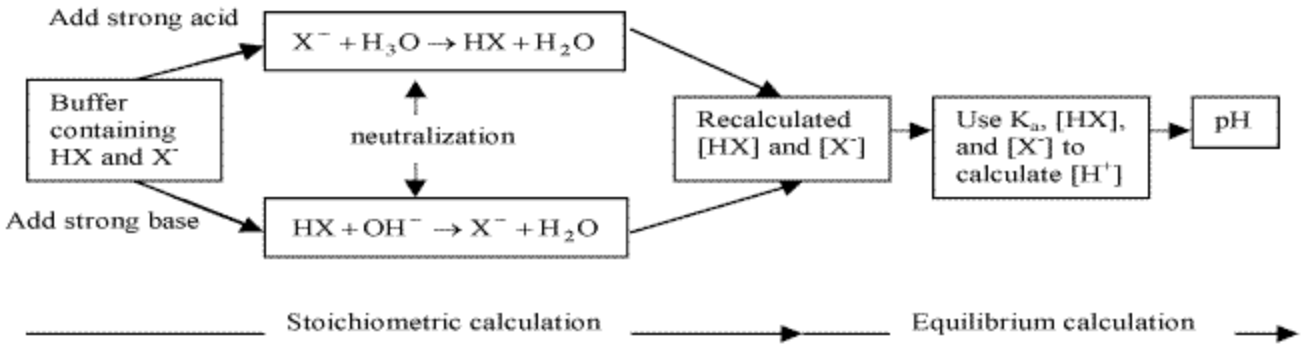
- buffer capacity – amount of acid or base buffer can neutralize before the pH changes considerably
- capacity depends on amount of acid or base in buffer
- pH depends on K_a for acid and relative concentrations of the acid and base
- Henderson-Hasselbalch Approximation:

$$pH = pK_a + \log_{10} \frac{[base]}{[acid]}$$

- [base] and [acid] = concentrations of conjugate acid-base pair
- when [base]=[acid], pH = pK_a
- can use initial concentrations of acid and base components of buffer directly into equation

17.2.3 Addition of Strong Acids or Bases to Buffers

reactions between strong acids and bases go to completion



Buffer contain HX and X minus. Add strong acid or strong bass for neutralization. Recalculate the concentrations. Use Ka to calculate the concentration of H plus and use that to get pH.

Either strong base or acid assumed to be completely consumed by reaction with buffer if buffering capacity is not exceeded

17.3: Acid-Base Titrations

- solution containing a known [base] added to an acid or acid solution added to base
- acid-base indicators used to signal equivalence point
- titration curve – pH vs Volume

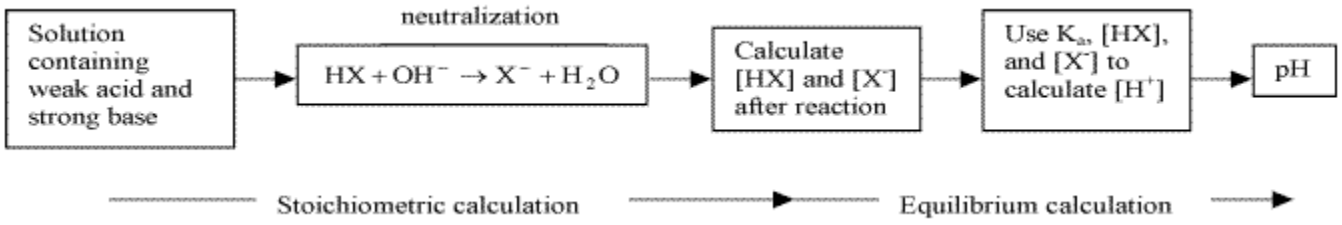
17.3.1 Strong Acid – Strong base Titrations

- pH starts out low ends high
- pH before equivalence point is pH of acid not neutralized by base
- pH at equivalence point is pH of solution
- pH equals 7.00
- for strong base titrations, the pH starts high ends low

17.3.2 The Addition of a Strong Base to a Weak Acid

Reactions between weak acid and strong base goes to completion

- calculating pH before equivalence point
  - stoichiometric calculations: allow strong base to react to completion producing a solution containing a weak acid and its conjugate base



Start with solution contain weak acid and strong base. Go through neutralization. Calculate the concentrations after the reaction. Use Ka to and concentrations to calculate the concentration of H plus. Use H plus to figure out pH.

  - equilibrium calculation: use K_a and equilibrium expression to find equilibrium concentrations of the weak acid and its conjugate base, and H^+

17.3.3 Titration Curves for Weak Acids or Weak Bases

Differences between strong acid-strong base titrations

1. solution of weak acid as higher initial pH than solution of a strong acid with same concentration
2. solution of weak acid rises more rapidly in early part of titration and more slowly as it reached the equivalence point
3. pH is not 7.00 at equivalence point

- before equivalence point solution has mixture of weak acid and its salt
- also called the buffer region of curve
- at equivalence point solution contains only salt
- weakly basic due to hydrolysis of anion
- after equivalence point solution has mixture of salt and excess strong base
- pH determined by [base]

17.3.4 Titrations of Polyprotic Acids

- reaction occurs in series of steps
- titration curve shows multiple equivalence points

17.4: Solubility Equilibria

17.4.1 The Solubility-Product Constant, K_{sp}

- saturated solution – dissolved and undissolved solute are at equilibrium
- expressed by g/L
- molar solubility – moles of solute dissolved to form a liter of saturated solution (mol/L)
- K_{sp} equilibrium constant for the equilibrium between an ionic solid and its saturated solution
- Solubility of compound (g/L) à molar solubility of compound (mol/L) à [molar] of ions à K_{sp} of ions

17.5: Factors that Affect Solubility

solubility affected by temperature and presence of other solutes. The solubility of ionic compound affected by:

- the presence of common ions
- pH of solution
- presence of complexing agent

17.5.1 Common-Ion Effect

- solubility of slightly soluble salt decreases when a second solute has a common ion

17.5.2 Solubility and pH

- solubility of any ionic compound affected if solution is acidic or basic
- change only noticeable if both ions are moderately acidic or basic
- solubility of slightly soluble salts containing basic anions increase as $[H^+]$ increases (as pH is lowered)
- the more basic an anion is, the greater the solubility will be affected by pH

17.5.3 Formation of Complex Ions

- metal ions act as Lewis acids in water
- complex ion – metal ion and Lewis base bonded together
- K_f – formation constant, equilibrium expression for formation of a complex ion
- Solubility of metal salts increases in acceptable Lewis bases if metal forms a complex base
- Lewis bases: NH_3, CN^-, OH^-

17.5.4 Amphoterism

- amphoteric substances include hydroxides and oxides of: Al^{3+}, Cr^{2+}, Zn^{2+}, and Sn^{2+}
- dissolve in strongly basic solutions
- formation of complex anions containing, typically four, hydroxides bound to metal ion
- amphoterism also associated with behavior of water molecules that surround and bond to metal ions by Lewis acid-base interactions

17.6: Precipitation and Separation of Ions

Q = ion product

- If Q > K_{sp}, precipitation occurs until Q = K_{sp}
- If Q = K_{sp}, equilibrium exists, have a saturated solution
- If Q < K_{sp}, solid dissolves until Q = K_{sp}

17.6.1 Selective Precipitation of Ions

- separation of ions in aqueous solution using a reagent that precipitates only with selected ions

17.7: Qualitative Analysis for Metallic Elements

Qualitative analysis: determines presence or absence of a particular metal ion

- ions separated into broad groups on basis of solubility
- ions separated by dissolving selected members in group
- ions identified by specific tests

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18: CHEMISTRY OF THE ENVIRONMENT

Environmental chemistry is the scientific study of the chemical and biochemical phenomena that occur in natural places. It should not be confused with green chemistry, which seeks to reduce potential pollution at its source.

18.1: Earth's Atmosphere

18.2: Outer Regions of the Atmosphere

18.3: Ozone in the Upper Atmostphere

18.4: Chemistry of the Troposphere

18.5: The World Ocean

18.6: Fresh Water

18.7: Green Chemistry

18.E: Chemistry of the Environment (Exercises)

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18.1: Earth's Atmosphere

Discussion Questions

- How do atmospheric scientists view the atmosphere?
- What gases are pollutants in the atmosphere?

The atmospheric chemistry studies the chemical composition of the natural atmosphere, the way gases, liquids, and solids in the atmosphere interact with each other and with the earth's surface and associated biota, and how human activities may be changing the chemical and physical characteristics of the atmosphere. It is interesting to note that the 1995 Nobel Prize in Chemistry 1995 was awarded to the atmospheric scientists P. Crutzen, M. Molina and F. S. Rowland. For convenience of study, atmospheric scientists divide the atmosphere as if it consists of four layers. The division is mainly due to temperature variations as the altitude increases. The four layers according to the variation of temperature are.

- Ionosphere (Aurora) or Thermosphere
- Mesosphere
- Stratosphere
- Troposphere

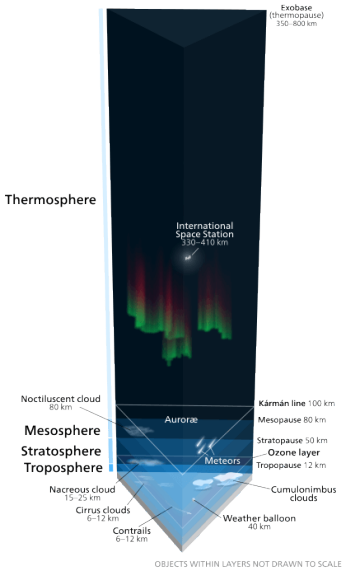


Figure 18.1.1: Earth's atmosphere Lower 4 layers of the atmosphere in 3 dimensions as seen diagonally from above the exobase. Layers drawn to scale, objects within the layers are not to scale. Aurorae shown here at the bottom of the thermosphere can actually form at any altitude in this atmospheric layer. from NASA.

Above 100 km is the thermosphere and ionosphere where the temperature increases from 200 K at 100 km to 500 K at 300 km. The temperature goes even higher as the altitude increases. activity as the altitude decrease. In the outer space, most particles consist of single atoms, H, He, and O etc. At lower altitude (200 - 100 km), diatomic molecules N_2, O_2, NO etc are present. The ionosphere is full of electrically charged ions. The UV rays ionizes these gases. The major reactions are

In the ionosphere:

$$O + hv \rightarrow O^+ + e^- \tag{18.1.1}$$

$$N + hv \rightarrow N^+ + e^- \tag{18.1.2}$$

In the neutral thermosphere:

$$N + O_2 \rightarrow NO + O \tag{18.1.3}$$

$$N + NO \rightarrow N_2 + O \tag{18.1.4}$$

$$O + O \rightarrow O_2 \tag{18.1.5}$$

Beyond the neutral thermosphere is the ionosphere and exosphere. These layers are of course interesting for space explorations and environmental concerns and space sciences. The atmosphere in the outer space is more like a plasma than a gas. Below the thermosphere is the mesosphere (100 - 50 km) in which the temperature decreases as the altitude increase. In this region, OH, H, NO, HO_2, O_2, and O_3 are common, and the most prominent chemical reactions are:

$$H_2O + h\nu \rightarrow OH + H \tag{18.1.6}$$

$$H_2O_2 + O \rightarrow OH + OH. \tag{18.1.7}$$

Below the mesosphere is the **stratosphere**, in which the temperature increases as the altitude increase from 10 km to 50 km. In this region, the following reactions are common:

$$NO_2 \rightarrow NO + O \tag{18.1.8}$$

$$N_2O \rightarrow N_2 + O \tag{18.1.9}$$

$$H_2 + O \rightarrow OH + H \tag{18.1.10}$$

$$CH_4 + O \rightarrow OH + CH_3 \tag{18.1.11}$$

Air flow is horizontal in the stratosphere. A thin ozone layer in the upper stratosphere has a high concentration of ozone. This layer is primarily responsible for absorbing the ultraviolet radiation from the sun. The ozone is generated by these reactions:

$$O_2 + h\nu \rightarrow O + O \tag{18.1.12}$$

$$O_2 + O \rightarrow O_3 \tag{18.1.13}$$

The troposphere is where all weather takes place; it is the region of rising and falling packets of air. The air pressure at the top of the troposphere is only 10% of that at sea level (0.1 atmospheres). There is a thin buffer zone between the troposphere and the next layer called the tropopause.



Figure 18.1.2: Space Shuttle Endeavour silhouetted against the atmosphere. The orange layer is the troposphere, the white layer is the stratosphere and the blue layer is the mesosphere.[1] (The shuttle is actually orbiting at an altitude of more than 320 km (200 mi), far above all three layers.). from NASA.

The major components in the region close to the surface of the Earth are N_2 (78%), O_2 (21%), Ar (1%) with variable amounts of H_2O, CO_2, CH_4, NO_2, NO_2, CO, N_2O, and O_3. The ozone concentration in this layer is low, about 8% of the total ozone in the atmosphere is in the troposphere.

What gases are pollutants in the atmosphere?

From the atmospheric science viewpoint, interactions of all gasses among themselves and their interaction with the environmental elements are of interest. However, for identification purposes, we need to identify the gases produced by man-made process (industry).

Some of the gases due to human activities are:

- Carbon dioxide result from the excess burning of carbon-containing fuel.
- Carbon monoxide produced by automobiles. This orderless and colorless gas is very toxic.
- Ozone produced in the exhaust of internal combustion engine, and the variation of ozone concentration in the stratosphere.
- Nitrogen oxides such as NO, NO_2, N_2O_4; due to the production of NO in the internal combustion engine.
- Methane gas produced due to treatments of large amount of waste.
- Sulfur oxides produced in mining operation and in the combustion of sulfur containing fuel. Sulfur oxide causes the so called *acid rain* problem.
- Chlorofluorocarbons (CFC) are gases used as refrigerant. When disposed into the atmosphere, they cause the ozone concentration to decrease.

Water vapor is also considered a greenhouse gas, but it is also generated by nature continuously due to radiation from the Sun. Of course, when water vapor condense into a liquid, much energy is released in the exothermal process. Condensation of water vapor causes storms and many of the weather phenomena.

Questions

1. According to what is the atmosphere divided into 4 layers?

   Skill -

   Describe the structure of the atmosphere.
2. Which layer contains the most ozone?

   Skill - Describe all the details of ozone?

3. How thick is the troposphere?

   Discussion - At the top of the world highest mountain, ~10 km in altitude, the atmosphere is only 0.1 of that at sea level. This is the top of the troposphere.

4. What type of gas is present in the thermosphere?

   Skill - Explain the chemistry taken place in the thermosphere?

5. How is the ionosphere different from other layers?

   Discussion - The aurora is related to the ions in the atmosphere.

6. What causes the gas molecules in the ionosphere to ionize and become charged particles?

   Skill - Describe the chemistry in the ionosphere.

7. If ozone is a beneficial gas in the atmosphere, why is ozone also a gaseous pollutant?

   Discussion - Decomposition of ozone releases O, OOH, OH radicals and they are harmful to many living organisms.

8. Why are chlorofluorocarbons a gases pollutant?

   Discussion - Ozone in the stratosphere absorbs harmful UV C and UV B, which are harmful to humans and plants.

9. Why is warming up of the Earth a bad thing?

Skill - Give your opinion please on an issue.

Solutions

1. The division is made according to patterns of temperature variation.
2. The stratosphere, between 15 and 50 km.
3. The troposphere ranges from 8 to 15 km.
4. A very dilute concentration of monoatomic gas.
5. The ionosphere contains high concentration of charged particles.
6. Radiation or high energy photons from the sun caused ionization of atoms.
7. Ozone is very reactive, causing harm to living organisms.
8. Because they catalyze the decomposition of ozone in the stratosphere.
9. Because we do not know what is the consequence in the future.

Learning Guide

- How is the atmosphere divided into layers? What are the names of the layers?
- Where is the ozone layer located in the atmosphere? What is the molecular structure of ozone? How is the ozone formed?

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18.2: Outer Regions of the Atmosphere

The mesosphere starts just above the stratosphere and extends to 85 kilometers (53 miles) high. Temperatures in the **mesosphere** decrease with altitude. Because there are few gas molecules in the mesosphere to absorb the Sun's radiation, the heat source is the stratosphere below. The mesosphere is extremely cold, especially at its top, about -90 degrees C (-130 degrees F).

The air in the mesosphere has extremely low density: 99.9 percent of the mass of the atmosphere is below the mesosphere. As a result, air pressure is very low. A person traveling through the mesosphere would experience severe burns from ultraviolet light since the ozone layer which provides UV protection is in the stratosphere below. There would be almost no oxygen for breathing. Stranger yet, an unprotected traveler's blood would boil at normal body temperature because the pressure is so low. Meteors burn up in this layer.

The thermosphere starts just above the mesosphere and extends to 600 kilometers (372 miles) high. Thermosphere is taken from the Greek word thermos which means heat. The density of molecules is so low in the **thermosphere** that one gas molecule can go about 1 km before it collides with another molecule. Since so little energy is transferred, the air feels very cold.

Within the thermosphere is the **ionosphere**. The ionosphere gets its name from the solar radiation that ionizes gas molecules to create a positively charged ion and one or more negatively charged electrons. The freed electrons travel within the ionosphere as electric currents. This dynamic region grows and shrinks based on solar conditions and divides further into the sub-regions: D, E and F; based on what wavelength of solar radiation is absorbed. The ionosphere is a critical link in the chain of Sun-Earth interactions.

Because of the free ions, the ionosphere has many interesting characteristics. At night, radio waves bounce off the ionosphere and back to Earth. This is why you can often pick up an AM radio station far from its source at night.The Van Allen radiation belts are two doughnut-shaped zones of highly charged particles that are located beyond the atmosphere in the **magnetosphere**. The particles originate in solar flares and fly to Earth on the solar wind. Once trapped by Earth's magnetic field, they follow along the field's magnetic lines of force. These lines extend from above the equator to the North Pole and also to the South Pole then return to the equator.

When massive solar storms cause the Van Allen belts to become overloaded with particles, the result is the most spectacular feature of the ionosphere — the **aurora**. The particles spiral along magnetic field lines toward the poles. The charged particles energize oxygen and nitrogen gas molecules, causing them to light up. Each gas emits a particular color of light.

There is no real outer limit to the **exosphere**, the outermost layer of the atmosphere; the gas molecules finally become so scarce that at some point there are no more. Beyond the atmosphere is the solar wind. The solar wind is made of high-speed particles, mostly protons and electrons, traveling rapidly outward from the Sun.

Figure 18.2.1 *The Earth's atmosphere* ***Credit:*** *NASA/Goddard*

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18.3: Ozone in the Upper Atmostphere

Discussion Questions

- What is UV?
- How is ozone produced in the atmosphere?
- How much ozone is in the atmosphere, and where is the ozone layer?
- What is the interaction of ozone and UV?
- What is ozone depletion?
- What is ozone hole and how does it vary over time?
- What are CFCs?
- How do CFCs help depleting ozone?
- How is ozone depletion in the polar region different from other regions?
- What has been done and what can be done to reduce ozone depletion?

Most of the ozone in the atmosphere is in the stratosphere of the atmosphere, with about 8% in the lower troposphere. As mentioned there, the ozone is formed due to photo reaction. The ozone level is measured in Dobson Unit (DU), named after G.M.B. Dobson, who investigated the ozone between 1920 and 1960. One Dobson Unit (DU) is defined to be 0.01 mm thickness of ozone at STP when all the ozone in the air column above an area is collected and spread over the entire area. Thus, 100 DU is 1 mm thick.

What is UV?

In the electromagnetic radiation spectrum, the region beyond the violet (wavelength ~ 400 nanometer nm) invisible to eye detection is called ultraviolet (UV) rays. Its wavelength is shorter than 400 nm.

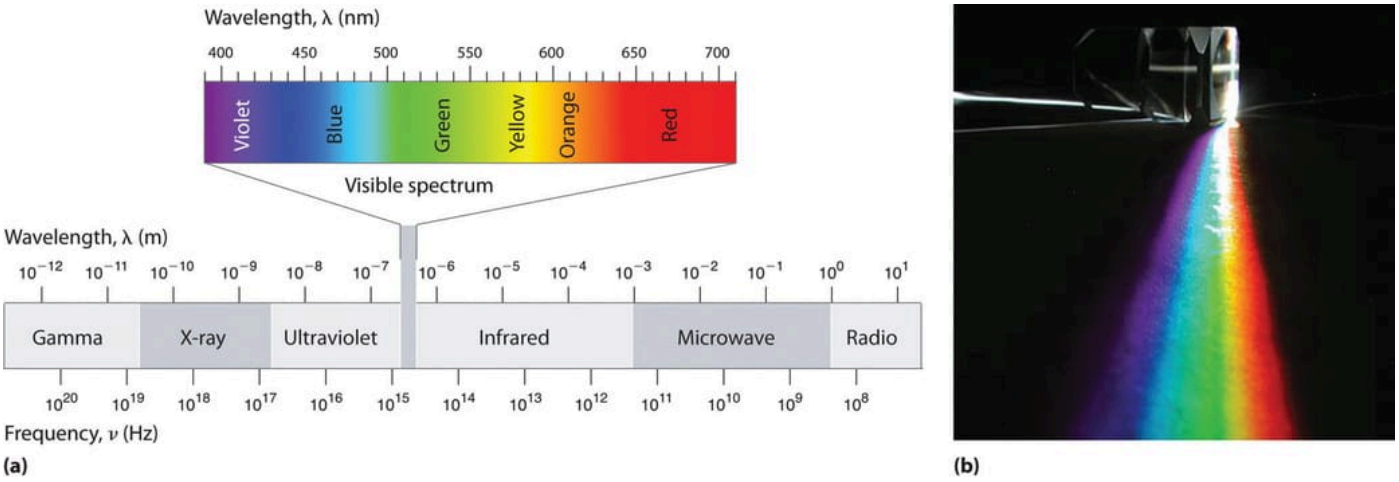


Figure 18.3.1: (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

UV is divided into three regions:

- UV A, wavelength = 400 - 320 nm
- UV B, wavelength = 320 - 280 nm
- UV C, wavelength = < 280 nm

Obviously, photons of UV C are the most energetic. UV-A radiation is needed by humans for the synthesis of vitamin-D; however, too much UV-A causes photoaging (toughening of the skin), suppression of the immune system and, to a lesser degree, reddening of the skin, and cataract formation. Ozone strongly absorbs UV B and C, but the absorption decreases as the wavelength increases

to 320 nm. Very little UV C reaches the Earth surface due to ozone absorption.

How is Ozone produced in the Atmosphere?

When an oxygen molecule receive a photon (h\nu), it dissociates into monoatomic (reactive) atoms. These atoms attack an oxygen molecule to form ozone, O3.

$$\mathrm{O_2 + h\nu \rightarrow O + O} \tag{18.3.1}$$

$$\mathrm{O_2 + O \ \rightarrow O_3} \tag{18.3.2}$$

The last reaction requires a third molecule to take away the energy associated with the free radical $O^{\cdot}$ and O_2, and the reaction can be represented by

$$\mathrm{O_2 + O + M \ \rightarrow O_3 + M \cdot} \tag{18.3.3}$$

The over all reaction between oxygen and ozone formation is:

$$\mathrm{3\,O_2 \ \rightleftharpoons 2\,O_3} \tag{18.3.4}$$

The absorption of UV B and C leads to the destruction of ozone

$$\mathrm{O_3 + h\nu \rightarrow O + O_2} \tag{18.3.5}$$

$$\mathrm{O_3 + O \ \rightarrow 2\,O_2} \tag{18.3.6}$$

A dynamic equilibrium is established in these reactions. The ozone concentration varies due to the amount of radiation received from the sun.

18.3.1

The enthalpy of formation of ozone is 142.7 kJ / mol. The bond energy of O2 is 498 kJ / mol. What is the average O=O bond energy of the bent ozone molecule O=O=O?

Solution

The overall reaction is

$$\mathrm{3\,O_2 \ \rightarrow 2\,O_3} \quad \Delta H = 286kJ \tag{18.3.7}$$

Note that 3 O=O bonds of oxygen are broken, and 4 O-O bonds of ozone are formed. If the bond energy of ozone is *E*, then

$$\begin{aligned} E &= (3 * 498 + 286)kJ/4mol \\ &= 445kJ/mol \end{aligned}$$

DISCUSSION
The ozone bonds are slightly weaker than the oxygen bonds. The average bond energy is not the bond energy for the removal of one oxygen from ozone.

$$\mathrm{O_3 + h\nu \rightarrow O + O_2} \tag{18.3.8}$$

Can the energy to remove one oxygen be estimated from the data given here?

The techniques used in this calculation is based on the **principle of conservation of energy**.

Example 18.3.2

The bond energy of O2 is 498 kJ / mol. What is the maximum wavelength of the photon that has enough energy to break the O=O bond of oxygen?

Solution

The energy per O=O bond is:

$$(498000J/mol)/(6.022x1023bonds/mol) = 8.27x10 - 19J/bonds \tag{18.3.9}$$

The wavelength λ of the photons can be evaluated using

$$E = \frac{hc}{\lambda} \tag{18.3.10}$$

$$\lambda = \frac{(6.626 \times 10^{-34}\, J \cdot s) * (3 \times 10^{8}\, m/s)}{8.27 \times 10^{-19} J}$$
$$= 2.403 \times 10^{-7}\, m = 240nm$$

DISCUSSION

The visible region range from 300 nm to 700 nm, and radiation with a wavelength of 240 nm is in the ultraviolet region (Figure 18.3.1). Visible light cannot break the O=O bond, and UV light has enough energy to break the O=O bond.

Chlorofluorohydrocarbons (CFCs)

Chemist Roy J. Plunkett discovered tetrafluoroethylene resin while researching refrigerants at DuPont. Known by its trade name, Teflon, Plunkett's discovery was found to be extremely heat-tolerant and stick-resistant. After ten years of research, Teflon was introduced in 1949. His continued research led to the usage of chlorofluorohydrocarbons known as CFCs or freon as refrigerants.

CFCs are made up of carbon, hydrogen, fluorine, and chlorine. DuPont used a number system to distinguish their product based on three digits. The digits are related to the molecular formulas.

- The first digit is the number of carbon atoms minus 1.
- The second digit is the number of hydrogen atoms plus 1.
- The third digit is the number of fluorine atoms minus 1.

For example, CFC (or freon) 123 should have a formula $C_2HF_3Cl_2$. The number of chlorine atoms can be deduced from the structural formula of saturated carbon chains. CFC's containing only one carbon atom per molecule has only two digits. Freon 12 used for fridge and automobil air conditioners has a formula of CF_2Cl_2. The nontoxic and nonflammable CFCs have been widely used as refrigerants, in aerosol spray, and dry cleaning liquid, foam blowing agents, cleansers for electronic components in the 70s, 80s and early 90s.

In 1973, James Lovelock demonstrated that all the CFCs produced up to that time have not been destroyed, but spread globally throughout the troposphere. (Lovelock's report was later published: J. E. Lovelock, R.J.Maggs, and R.J. Wade, (1974); *Nature*, **241**, 194) In the article, concentrations of CFCs at some parts per 10^{11} by volume was measured, and they deducted that with such a concentration, CFCs are not destroyed over the years. In 1974, Mario J. Molina published an article in *Nature* describing the ozone depletion by CFCs. (see M.J. Malina and F.S. Rowland, (1974); *Nature*, **249**, 810) NASA later confirmed that HF was present in the stratosphere, and this compound had no natural source but from the decomposition of CFCs. Molina and Rowland suggested that the chlorine radicals in CFCs catalyze the decomposition of ozone as discussed below.

How do CFCs help depleting ozone?

A relatively recent concern is the depletion of ozone, O3 due to the presence of chlorine in the troposphere, and eventually their migration to the stratosphere. A major source of chlorine is Freons: CFCl3 (Freon 11), CF2Cl2 (Freon 12), C2F3Cl3 (Freon 113),

C2F4Cl2 (Freon 114). Freons decompose in the troposphere. For example,

$$\mathrm{CFCl_3} \rightarrow \mathrm{CFCl_2 + Cl} \tag{18.3.11}$$

$$\mathrm{CF_2Cl_3} \rightarrow \mathrm{CF_2Cl + Cl^{\bullet}} \tag{18.3.12}$$

The chlorine atoms catalyze the decomposition of ozone,

$$\mathrm{Cl + O_3} \rightarrow \mathrm{ClO + O_2} \tag{18.3.13}$$

and ClO molecules further react with O generated due to photochemical decomposition of ozone:

$$\mathrm{O_3 + h\nu \rightarrow O + O_2} \tag{18.3.14}$$

$$\mathrm{ClO + O} \rightarrow \mathrm{Cl + O_2} \tag{18.3.15}$$

$$\mathrm{O + O_3} \rightarrow \mathrm{O_2 + O_2 \cdot} \tag{18.3.16}$$

The net result or reaction is

$$\mathrm{2\,O_3} \rightarrow \mathrm{3\,O_2} \tag{18.3.17}$$

Thus, the use of CFCs is now a world wide concern. In 1987, one hundred and forty nine (149) nations signed the Montreal Protocol. They agreed to reduce the manufacturing of CFCs by half in 1998; they also agree to phase out CFCs.

Ozone depletion in the polar region is different from other regions. The debate of ozone depletion often involves the North and South Poles. In these regions when temperatures drop to 190 K, ice cloud is formed. The ice crystals act as heterogeneous catalyst converting HCl and $ClONO_2$ into HNO_3 and Cl_2,

$$\mathrm{Cl + ClONO_2} \rightarrow \mathrm{HNO_3 + Cl_2} \tag{18.3.18}$$

$$\mathrm{H_2O + ClONO_2} \rightarrow \mathrm{HNO_3 + HOCl \cdot} \tag{18.3.19}$$

Both Cl_2, and HOCl are easily photolyzed to Cl atoms, which catalyze the depletion of ozone. This has just been discussed in the previous section.

What has been done and what can be done to reduce ozone depletion?

The U.S. and Canadian governments have banned the use of Freons in aerosol sprays, but their use in air conditioner and cooling machines continue. In order to eliminate Freon in the atmosphere, international concerted effort and determination is required. However, sound and reliable scientific information is required. The banning of CFCs opens a research opportunity for another invention to find its substitute. Who knows what other problems will the new product bring?

Questions

1. **What is the unit used for measuring ozone layers?**

   Skill - Define a unit you use.

2. **What is the wavelength range of the UV radiation?**

   Skill - Describe UV radiation.

3. **How is ozone different from oxygen?**

   Skill - Describe the formation of ozone.

4. **When CFCs are exposed to UV or sun light, what species are produced?**

   Skill - Explain a photodecomposition reaction.

5. **What is the role of chlorine radical in the ozone formation or reactions.**

   Skill - Explain the mechanism of the catalytic reaction.

6. **What in the polar zone makes the depletion of ozone more serious?**

Solutions

1. Dobson unit.
2. UV radiation is electromagnetic radiation with wavelength between 100 and 400 nm.
3. The ozone molecules consist of 3 atoms whereas the usual oxygen molecules 2.
4. Reactive radicals are produced, including monoatomic chlorine radical.
5. Chlorine radical catalyze the decomposition of ozone.
6. The ice clouds act as heterogeneous catalysts for the formation of chlorine gas.
   Discussion - The chlorine gas is photodissociated into Cl radicals that catalyze the decomposition of ozone.

Learning Guide

- Arrange the regions of the electromagnetic spectrum in increasing energies of their photons: X-rays, visible, gamma rays, ultraviolet, infrared, microwave, etc.
- Examples on this *page* can be testing questions.
- What are CFCs?
  What are freon 12, 123, and 114?
  Explain how CFC help destroy the atmosphere ozone layer, particularly the polar region?

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18.4: Chemistry of the Troposphere

A lot of chemistry happens in Earth's atmosphere; there are many different kinds of chemicals in the air. Those chemicals often combine with each other in chemical reactions, making new and different chemicals. This is called "atmospheric chemistry".

Earth's atmosphere has different layers. The lowest layer is called the troposphere. We live in the troposphere. This page explains about atmospheric chemistry in the troposphere.

Most of the gas in our atmosphere is nitrogen. About 4/5ths of the air is nitrogen. What about the other 1/5th? Almost all of it is oxygen, the stuff in the air we need to breathe. There are also very small amounts of a bunch of other chemicals.

Have you heard of greenhouse gases? They are kinds of gases that trap the heat from sunlight in our atmosphere. Earth would be very cold if we didn't have any greenhouse gases. Carbon dioxide and methane are two very important greenhouse gases.

Some of the chemicals in the air come from pollution. When we burn coal in a factory or gasoline in our cars, we make air pollution. Coal and oil have sulfur in them. When they burn, they make chemicals called sulfur oxides. These can turn into sulfuric acid when they mix with water droplets in the air. These droplets of acid can fall to the ground as acid rain. Cars and trucks also give off chemicals called nitrogen oxides. Nitrogen oxides combine with other chemicals to make smog. They also help make nitric acid, which is another acid in acid rain.

Nature also does things to change the chemistry of the troposphere. Volcanoes, lightning, and wildfires all add chemicals to the air or change the ones that are already there. Energy from sunlight can make chemical reactions happen, changing one gas into another. Some chemicals move in cycles between the atmosphere, living creatures, and the oceans. The Carbon Cycle and the Nitrogen Cycles are two important cycles that change the chemistry of the atmosphere.

This table (below) describes some of the chemicals in the troposphere, and some of the chemical reactions that happen in the air:

Chemicals in the troposphere, and some of the chemical reactions that happen in the air

Chemical	Formula	Role in Tropospheric Chemistry
Carbon dioxide	CO_2	Carbon dioxide is a kind of greenhouse gas. When we breathe, we take in oxygen and breathe out carbon dioxide. Plants and some kinds of microbes use carbon dioxide during photosynthesis to make food. Burning fuels also puts carbon dioxide into the atmosphere.
Carbon monoxide	CO	When things burn, they mostly make carbon dioxide. Sometimes they make carbon monoxide, too. Carbon monoxide is a poisonous gas. Volcanoes and car enginesmake carbon monoxide.
Hydrocarbons	C_xO_y	Hydrocarbons are chemicals made up of hydrogen and carbon atoms. When fuel burns, it puts some hydrocarbons into the air. Hydrocarbons help to make smog, a kind of air pollution.
Methane	CH_4	Methane is a kind of greenhouse gas.
Nitrogen	N_2	Most of the gas in Earth's atmosphere is nitrogen. About 4/5ths of the air is nitrogen. The nitrogen cycle explains how nitrogen moves around in the environment. When fuel burns hot, like it does in the engine of a car, nitrogen combines with oxygen to make nitrogen oxides.
Nitrogen Oxides	NO & NO_2	Nitrogen oxides are a kind of pollution. Burning fuels like gasoline in air makes nitrogen oxides. Most nitrogen oxides come from cars and trucks. They help to make smog. They also mix with water droplets in the air to make nitric acid. Nitric acid is a part of acid rain.
Nitric Acid	HNO_3	Nitric acid is part of acid rain. Nitric acid forms when nitrogen oxides mix with water droplets in the air. Nitrogen oxides are a kind of pollution that comes from the engines of cars and trucks.
Oxygen & Ozone	O_2 & O_3	About 1/5th of the gas in the atmosphere is oxygen. When you breathe, your body uses the oxygen to keep you alive. Ozone is a special kind of oxygen that has three atoms instead of two.
PAN(Peroxyacetyl nitrate)	$C_2H_3O_5N$	PAN is a kind of air pollution. Smog has PAN in it. PAN forms when nitrogen dioxide, oxygen, and Volatile Organic Compounds (VOCs) get together.

Chemical	Formula	Role in Tropospheric Chemistry
Smog	-	Smog is a mixture of smoke and fog. Photochemical smog is a kind of air pollution. It has nitrogen oxides, ozone, VOCs, and PAN in it.
Photodissociation	-	When a photon of sunlight breaks apart a molecule.
Sulfur Oxides	SO_2 & SO_3	Sulfur dioxide and sulfur trioxide are types of pollution. People make them when we burn coal and oil. Volcanoes also give off sulfur oxides. Sulfur dioxide mixes with water droplets in the air to make sulfuric acid. Sulfuric acid is in acid rain.
Sulfuric Acid	H_2SO_4	Sulfuric acid is in acid rain. Sulfuric acid in the air is made when sulfur dioxide gasmixes with water droplets. The sulfur dioxide gas comes from volcanoes and from coal and oil that people burn for fuel.

www.windows2universe.org/ear...oposphere.html

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18.5: The World Ocean

Discussion Questions

- What is hard water?
- What are the differences between temporary and permanent hard water?
- How can hard water be converted to soft water?
- How to produce deionized water?

Water is the most important resource. Without water life is not possible. From a chemical point of view, water, H_2O, is a pure compound, but in reality, you seldom drink, see, touch or use pure water. Water from various sources contains dissolved gases, minerals, organic and inorganic substances.

The Hydrosphere

The total water system surrounding the planet Earth is called the **hydrosphere**. It includes freshwater systems, oceans, atmosphere vapour, and biological waters. The Arctic, Atlantic, Indian, and Pacific oceans cover 71% of the Earth surface, and contain 97% of all water. Less than 1% is fresh water, and 2-3 % is ice caps and glaciers. The Antarctic Ice Sheet is almost the size of North America continent. These waters dominate our weather and climate, directly and indirectly affecting our daily lives. They cover 3.35×10^8 km^2. The four oceans have a total volume of 1.35×10^9 km^3.

- The sunlight dims by 1/10 for every 75 m in the ocean, and humans barely see light below 500 m. The temperature of almost all of the deep ocean is 4°C (277 K).
- The average ocean depth is 4 km, and the deepest point at the Mariana Trench is 10,912 m (35,802 ft), which compares to the height of 8.8 km for Mount Everest.

Hydrospheric processes are steps by which water cycles on the planet Earth. These processes include sublimation of ice, evaporation of liquid, transportation of moisture by air, rain, snow, river, lake, and ocean currents. All these processes are related to the physical and chemical properties of water, and many government agencies are set up to study and record phenomena related to them. The study of these processes is called **hydrology**

Among the planets, Earth is the only one in which there are solid, liquid and gaseous waters. These conditions are just right for life, for which water is a vital part. Water is the most abundant substance in the biosphere of Earth. Groundwater is an important part of the water system. When vapor is cooled, clouds and rain develop. Some of the rain percolate through the soil and into the underlying rocks. The water in the rocks is **groundwater**, which moves slowly.

A body of rock, which contains appreciable quantities of water, is called an **aquifier**. Below the **water table**, the aquifier is filled (or saturated) with water. Above the water table is the unsaturated zone. Some regions have two or more water tables. These zones are usually separated by water-impermeable material such as boulder and clay. Groundwater can be brought to the surface by drilling below the water table, and pumped out. The amount of water that can be pumped out depends on the structure of the aquifer. Little water is stored in tight granite layers, but large quantities of water are stored in limestone aquifier layers. In some areas, there are under ground rivers.

Table 18.5.1*: Ions in sea water*

Species	Cl^-	Na^+	SO_4^-	Mg^{2+}	Ca^{2+}	K^+	HCO_3^-	Br^-	Sr^{2+}	BO_4^{3-}	F^-	H_4SiO_4	H^+
mg/Kg	10,760	2,710	2,710	1,290	411	399	142	67	8	4.5	1.3	0.5-10	$10^{-8.35}$

Common Ions Present in Natural Water

Hydrology is also the study of how solids and solute interact in, and with, water. In this link, the compositions of seawater, composition of the atmosphere, compositions of rain and snow, and compositions of river waters and lake waters are given in details. Table 18.5.1 list the major ions present in seawater. The composition does vary, depending on region, depth, latitude,

and water temperature. Waters at the river mouths contain less salt. If the ions are utilized by living organism, its contents vary according to the populations of organisms.

Dust particles and ions present in the air are nucleation center of water drops. Thus, waters from rain and snow also contain such ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}. These cations are balanced by anions, HCO_3^{-}, SO_4^{-}, NO_2^{-}, Cl^{-}, and NO_3^{-}. The pH of rain is between 5.5 and 5.6. Rain and snow waters eventually become river or lake waters. When the rain or snow waters fall, they interact with vegetation, top soil, bed rock, river bed and lake bed, dissolving whatever is soluble. Bacteria, algae, and water insects also thrive. Solubilities of inorganic salts are governed by the kinetics and equilibria of dissolution. The most common ions in lake and river waters are the same as those present in rainwater, but at higher concentrations. The pH of these waters depends on the river bed and lake bed. Natural waters contain dissolved minerals. Waters containing Ca^{2+} and Mg^{2+} ions are usually called **hard water**.

Hard Water

Minerals usually dissolve in natural water bodies such as lakes, rivers, springs, and underground waterways (ground waters). Calcium carbonate, $CaCO_3$, is one of the most common inorganic compounds in the Earth crust. It is the ingredient for both calcite and aragonite. These two minerals have different crystal structures and appearance. This photograph shows crystals of typical Calcite.

Calcium-carbonate minerals dissolve in water, with a solubility product as shown below.

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad K_{sp} = 5 \times 10^{-9} \tag{18.5.1}$$

From the solubility product, we can (see example 1) evaluate the molar solubility to be 7.1×10^{-5} M or 7.1 mg/L (7.1 ppm of $CaCO_3$ in water). The solubility increases as the pH decrease (increase acidity). This is compounded when the water is saturated with carbon dioxide, CO_2. Saturated CO_2 solution contains carbonic acid, which help the dissolution due to the reaction:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \tag{18.5.2}$$

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^{-} \tag{18.5.3}$$

Because of these reactions, some natural waters contain more than 300 ppm calcium carbonates or its equivalents.

The carbon dioxide in natural water creates an interesting phenomenon. Rainwater is saturated with CO_2, and it dissolves limestones. When CO_2 is lost due to temperature changes or escaping from water drops, the reverse reaction takes place. The solid formed, however, may be a less stable phase called aragonite, which has the same chemical formula as, but a different crystal structure than that of calcite.

The rain dissolves calcium carbonate by the two reactions shown above. The water carries the ions with it, sips through the crack of the rocks. When it reached the ceiling of a cave, the drop dangles there for a long time before fallen. During this time, the carbon dioxide escapes and the pH of the water increases. Calcium carbonate crystals begin to appear. Calcite, aragonite, stalactite, and stalagmite are four common solids found in the formation of caves.

Natural waters contain metal ions. Water containing calcium, magnesium and their counter anions are called **hard waters**. Hard waters need to be treated for the following applications.

- Heat transfer carrier in boilers and in cooling systems
- Solvents and reagents in industrial chemical applications
- Domestic water for washing and cleaning

Temporary vs. Permanent Hard Water

Due to the reversibility of the reaction,

$$CaCO_{3(s)} + H_2CO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^{-} \tag{18.5.4}$$

water containing Ca^{2+}, Mg^{2+} and CO_3^{2-} ions is called **temporary hard water**, because the hardness can be removed by boiling.

Boiling drives the reverse reaction, causing deposit in pipes and scales in boilers. The deposits lower the efficiency of heat transfer in boilers, and diminish flow rates of water in pipes. Thus, temporary hard water has to be softened before it enters the boiler, hot-water tank, or a cooling system. The amount of metal ions that can be removed by boiling is called **temporary hardness**

After boiling, metal ions remain due to presence of chloride ions, sulfate ions, nitrate ions, and a rather high solubility of $MgCO_3$. Amount of metal ions that can not be removed by boiling is called **permanent hardness. Total hardness** is the sum of temporary hardness and permanent hardness. Hardness is often expressed as equivalence of amount of calcium ions in the solution. Thus, water conditioning is an important topic. The value of water treatment market has been estimated to be worth $30 billion.

Lime-soda Softening

Lime-soda softening is the removal of temporary hardness by adding a calculated amount of hydrated lime, $Ca(OH)_2$:

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_{2(s)} \rightarrow 2CaCO_{3(s)} + 2H_2O \tag{18.5.5}$$

Adding more lime causes the pH of water to increase, and as a result, magnesium ions are removed by the reaction:

$$Mg^{2+} + Ca(OH)_{2(s)} \rightarrow Mg(OH)_{2(s)} + Ca^{2+} \tag{18.5.6}$$

The extra calcium ions can be removed by the addition of sodium carbonate.

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-} \tag{18.5.7}$$

$$Ca^{2+} + CO_3^{2-} + \rightarrow CaCO_{3(s)} \tag{18.5.8}$$

In this treatment, the amount of $Ca(OH)_3$ required is equivalent to the temporary hardness plus the magnesium hardness. The amount of sodium carbonate required is equivalent to the permanent hardness. Thus, lime-soda softening is effective if both the temporary and total hardness have been determined. The sodium ion will remain in the water after the treatment. The pH of the water is also rather high depending on the amount of lime and sodium carbonates used.

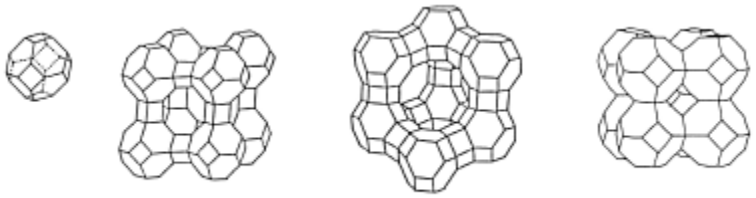
Complexation Treatment

Addition of complexing reagent to form soluble complexes with Ca^{2+} and Mg^{2+} prevents the formation of solid. One of the complexing agents is sodium triphosphate Na_3PO_4, which is marketed as Calgon, etc. The phosphate is the complexing agent. Other complexing agents such as Na_2H_2EDTA can also be used, but the complexing agent $EDTA^{4-}$ forms strong complexes with transition metals. This causes corrosion problem, unless the pipes of the system are made of stainless steel.

Ion Exchange

Today, most water softeners are using zeolites and employing ion exchange technique to soften hard water. Zeolites are a group of hydrated crystalline aluminosilicates found in certain volcanic rocks. The tetrahedrally coordinated aluminum and silicon atoms form AlO_4 and SiO_4 tetrahedral groups. They interconnect to each other sharing oxygen atoms forming cage-type structures as shown on the right. This diagram and the next structural diagram are taken from an introduction to zeolites There are many kinds of zeolites, some newly synthesized.

Whatever kind, the crystal structure of zeolites contains large cages. The cages are connected to each other forming a framework with many cavities and channels. Both positive and negative ions can be trapped in these cavities and channels as shown below.



For each oxygen that is not shared in the AlO_4 and SiO_4 tetrahedral groups, a negative charge is left on the group. These negative charges are balanced by trapping alkali metal and alkaline earth metal ions. When more cations are trapped, hydroxide and chloride ions will remain in the cavities and channels of the zeolites.

To prepare a zeolite for water treatment, they are soaked in concentrated NaCl solution. The cavities trap as many sodium ions as they can accommodate. After the treatment, the zeolite is designated as Na-zeolite. Then the salt solution is drained, and the zeolite is washed with water to eliminate the extra salt. When hard water flow through them, calcium and magnesium ions will be trapped by the Na-zeolite. For every Ca^{2+} or Mg^{2+} trapped, two Na^+ ions are released. The treated water contains a rather high concentration of Na^+ ions, but low concentrations of Mg^{2+} and Ca^{2+}. Thus, zeolite ion exchange convert hard water into soft water.

Pure Water by Ion Exchange

In most cases, the resins are polystyrene with functional $-SO_3H$ groups attached to the polymer chain for cation exchange resin, and with functional group $-N(CH_3)_3^+$ attached to the chain for anion exchange resin. To prepare the resin for making *pure or deionized water*, the cation resin is regenerated with HCl so that the groups are really $-SO_3H$. The anion resin is regenerated with NaOH, so that the functional groups are $-N(CH_3)_3(OH)$. When water containing any metal ion M^+ and anion A^- passes through the ion exchange resins in two stages, the following reactions take place,

$$M^+ + -SO_3H \rightarrow H^+ + -SO_3M \tag{18.5.9}$$

$$A^- + -N(CH_3)_3(OH) \rightarrow OH^- + -N(CH_3)_3A \tag{18.5.10}$$

$$H^+ + OH^- \rightleftharpoons H_2O \tag{18.5.11}$$

Thus, ion exchange provides *pure water* to meet laboratory requirement.

Reverse Osmosis Water Filter System

This method can also be used to prepare water for domestic and laboratory applications. This method has been discussed in Wastewater treatment

Magnetic Water Treatment

The following is a list of companies selling magnetic devices for **magnetic water treatment**. All devices are based on results of some ressearch indicating that when water runs through a magnetic field, the calcium carbonate will precipitate as aragonite rather than the usual calcite. For example, K.J. Kronenberg has published an article in *IEEE Transactions on Magnetics*, (Vol. Mag-21, No. 5, September 1985, pages 2059-2061). and stated the following:

> *The crystallization mode of the water's mineral content was found to change from a dendritic, substrate-bound solidification habit to the form of separate disc-shaped crystals after the water had moved through a number of magnetic fields. The former scarcity of crystallization nucleii in the water had been turned into an abundance of nucleation centers in the water. The reduction of the number of the substrate-bound crystals has been used as a quantitative measure of the magnetic effect.*

Many companies have made various devices for magnetic conditioning of water, and they claim that their devices will clean up the pipes and boilers at little or no cost. I have yet to test one of these devices for its claim, but my preliminary tests shows that permanent magnet has little effect on the calcium carbonate deposit of temporary hard water. The cleaning effect they have claimed is probably much overstated.

Example 18.5.1

From the solubility product shown for the dissolution of calcium carbonate,

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad K_{sp} = 5 \times 10^{-9} \tag{18.5.12}$$

Evaluate the molar solubility of Ca^{2+} in saturated solution.

Solution

From the definition of solubility product, we have

$$[Ca^{2+}][CO_3^{2-}] = 5 \times 10^{-9} \tag{18.5.13}$$

Thus,

$$[Ca^{2+}] = [CO_3^{2-}] = 7.1 \times 10^{-5}\ M \tag{18.5.14}$$

The concentration of 7.1×10^{-5} M is equivalent to 7.1 mg/L (7.1 ppm of $CaCO_3$ in water).

DISCUSSION

There may be other ions present in the system and other equilibria conditions in addition to the equilibrium mentioned here. Problems are more complexed in the real world.

Exercise 18.5.1

Boiling of 1.0 L of water produced 10 mg of CaCO3 solid. What is the temporary hardness of the water?

Answer available at the end of this section.

Contributors and Attributions

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Answers

Exercise 18.5.1

10 ppm

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18.6: Fresh Water

Discussion Questions

- Is water the source of life, why?
- What is life?
- Is life a symbiotic system of many lives?
- What properties of water make water the prime ingredient of life?
- What are the essential substances of life?
- Other than material, what else is essential for life?
- What is the role of water in supporting life?
- Is there a life form involving no water?
- Is there a method to determine the total water content?

Not finished yet, but the major ideas are here now!

Water Biology



Chemical and physical properties of water discussed in other pages are essential considerations for water biology. Natural water also contains biological matters as well as living creatures. In the discusssion of biology and water, you must feel pleasant, because they make each other grow more lovely as this picture from water lily cottage. The water pages of National Wildlife Federation, offers some interesting reading too.

All living things have a cycle of life. A cycle involves all or some of these process: birth, growth, mature, reproduction, matamorphosis, and death. There are millions of living organisms on Earth, ranging from single-cell amebas, bacteria, to the complicated homosapiens. There are also viruses which are fragment of DNA or RNA that depend on host cells for their reproduction. They are not cells.

Living things usually have cells that isolate their systems so that the cells contain unique materials to sustain the lives of cells. Cells regulate their contents (homeostatic), and carry out their metabolsims. They divide or making copies of themselves. Many reproduction process involve two individuals and future populations are subject to a greater diversity. Mutation is a fact of life, and many adopt to their changing environment.

How life started? Let the research and debate continue by not giving any clusive statements here. A physical geography course suggests that the marine invertebrates began their life 600 million years ago, and they are followed by fish, land plants, amphibians, reptiles, mommals, and then flowering plants, in this order. All these started more than a hundred million years ago,

and hominid (primate) line began its evolution 20 to 15 million years ago.

There are strong evidences that life on earth appeared in a body of water. Only the planet Earth has three states of water, and it offers a suitable environment for life to began, among all nine solar planets. Since all life forms involve water. Water is seen as the source, matrix, and mother of life. Water is important, because water is required for life, and some people even consider water as life blood.

Since water supports life, living organisms also modify their environment, changing the nature of the water in which they live. Biology of water pollution, lists the syllabus on a course including a laboratory section. Water and biology interweave into an entangled maze waiting for explorers and curious minds.

Water dissolves or emulsifies other life-supporting substances and transport them to intercellular and intracellular fluids. It is also a medium in which reactions take place. Reactions provide energy (non-matter) for living. Energy causes changes, and manifestation of changes is at least related to, if not the whole, life. An organized and systematized set of reactions is essential in each life.

Balancing Water in Bio-systems

Many living organisms live their lives entirely in water as shown here in this photo from a job center talking about work in marine biology. Aquatic living organisms extract neutrients from water, yet maintaining a balance of electrolyte and nurrishment concentration in their cells. For living things not living in water, they extract water from their environment by whatever mechanism they can. Cells in their body are surrounded by body fluid, and all cells maintain constant concentrations of electrolytes, neutrints, and metabolites. The process of maintaining constant concentrations is called homeostasis. Certainly, some active transport mechanisms are involved in this balance.

The rooting of every type of plants is unique. Generally speaking, plants having extensive roots are able to extract water under harsh conditions. On the other hand, some plants such as cactus, jade and juniper have little roots, but their leaves have a layer of wax that prevents water from evaporation. Water conserving plants tolerate draught, and they survive under harsh conditions. The picture shown here is a jade plant from the above link.

Lately, some pumpkin growers harvested squash weighing almost 500 kg. At the peak of the growing season, the squash grows almost 0.5 kg a day. That is equivalent to 25 moles of water collected by the roots, discounting the water evaporated through the leaves. The growth is particularly good during a hot and wet day, but during a hot sunny after noon, the temperature of the leaves and fruits get very hot.

Essential Electrolytes for Life Support

In addition to water, many inorganic substances or minerals are essential to life. These substances ionize in water to form ions and their solutions conduct electricity. Therefore, they are called **electrolytes**. Because most of these substances are already dissoved in natural water, we list ions instead of the mineral they come from.

When ions dissove, they form complexes with water molecules. For most metals, the first sphere of coordination usually involve 6 water molecules. For example, when sodium chloride dissolve, we have

$$\mathrm{NaCl} + 12\,\mathrm{H_2O} \rightleftharpoons \mathrm{Na(H_2O)_6}^{+} + \mathrm{Cl(H_2O)_6}^{-} \tag{18.6.1}$$

$$\mathrm{FeCl_2} + 18\,\mathrm{H_2O} \rightleftharpoons \mathrm{Fe(H_2O)_{62}}^{+} + 2\,\mathrm{Cl(H_2O)_6}^{-} \tag{18.6.2}$$

Formation of complexes are due to the high dipole moment of water, and the dissolution can be attribute to the high dielectric constant (80). However, in most publications, we ignore the water molecules in the complexes, and simply consider them as ions.

In the following, we describe some essential ions or salts as electrolytes.

- Sodium chloride, Na^+ and Cl^-
  NaCl is readily dissolved and absorbed in extracellular fluid. The two ions help to balance water, acid/base, osmotic pressure, carbon dioxide transport, and excreted in human urine and sweat. Lack of sodium chloride shows symptoms of dehydration.
- Potassium, K^+
  Good sources of potassium ions are vegetables, fruits, grains, meat, milk, and legumes. It is readily absorbed, and actively

transported into the intracellular fluid. Its function is similar to that of sodium ions, but cells prefer potassium ions over sodium. Lack of potassium leads to cardiac arrest.

- Calcium, Ca^{2+}
  Divalent calcium ions are usually poorly absorbed by human, but the are essential for the bones, teeth, blood clotting. Lack of calcium hinders growth and osteoporosis in old age.
- Phosphates, PO_4^{3-}
  Calcium phosphate is essential for bones, teeth, etc. However, phosphates are also responsible for many life reactions. ATP, NAD, FAD etc are metabolic intermediates, and they involve phosphate. Phospholipids and phosphoproteins are some other phosphate containing species.
- Magnesium, Mg^{2+}
  Magnesium ions are essential in chlorophyll. These ions are absorbed readily, and compete with calcium at times. Magnesium and calcium ions are present in hard water, and this link alerts the lack of magnesium leading to cardiovascular disease.
- Ferrous or ferric ions, Fe^{2+} or Fe^{3+}
  Usually known as iron, but iron are present either as divalent or as trivalent ions. Iron is absorbed according to body need; aided by HCl, ascorbic acid (vitamin C), and regulated by apoferritin. In mammals, iron is stored in liver as ferritin and hemosiderin. Iron deficiency leads to anemia. Good food sources of iron are liver, meats, egg yolk, green vegetables, and whole grains.
- Zinc ions, Zn^{2+}
  Zinc ions are important ingredients for many enzymes. They are present in insulin, carbonic anhydrase, carboxypeptidase, lactic dehydrogenase, alcohol dehydrogenase, alkaline phosphatase etc. Like iron, zinc deficiency leads to anemia and poor growth.
- Copper ions, Cu^{2+}
  Copper ions help iron utilization, and this metal is present in may enzymes.
- Cobalt ions, Co^{2+}
  Cobalt ions are centers of vitamin B12, and deficiency of which leads to anemia.
- Iondine ions, I^-
  Iondine is a constituent of thyroxin, which regulates cellular oxidation.
- Fluoride ions, F^-
  Fluoridation of drinking water is often a controversal issue. Childen's teeth are less seceptible to decay. Once they began to bruch their teeth, the fluoride in tooth paste is sufficient.

The eletrolytes listed above are present in significant amount in water, or fluids of organisms. There are some metals present in very minute quantities in biological systems, and these are not listed above.

Metal ions also interact with proteins. An **enzyme** is usually a very large protein molecule, and it folds into a kidney shape enclosing one or more metal ions forming a complex. The metal is usually responsible for the enzyme activity. Cobalt, copper, iron, molebdenium, nickel, and zinc have groups of enzymes each, and further discussion can be found in The Prosthetic groups and Metal Ions in Protein Active Sites Database (PROMISE). A general discussion is called **bioinorganic chemistry** and this site has an extensive General references on Bioinorganic Chemistry.

Balancing Electrolytes

Ions	Extracellular	Intracellular	Interstitial
Na^+	140	10	150
K^+	5	150	4
Ca^{2+}	10	4	6
Mg^{2+}	6	80	4
Total	**161**	**244**	**164**
Cl^-	103	2	120

Ions	Extracellular	Intracellular	Interstitial
$HCO3^-$	30	10	30
$HPO4^{2-}$	4	177	4
$SO4^{2-}$	2	10	2
Organic acid	6	5	6
Protein	16	40	2
Total	**161**	**244**	**164**

Electrolyte balance are maintained by **passive transport or diffusion and slective active transport mechanisms**. Diffusion process tends to make the concentration all the same throughout the entire fluid, but active or selective transport moves ions to special compartment. For example, the active transport of sodium and potasium by an enzyme called **sodium-potassium ATPase** is usually known as *sodium-potassium pump*. This process pumps potassium ions inside a cell while removing sodium ions from the cells. Thus, a high concentration of potassium is maintained inside cells. Energy is required in active transport, and cellular metabolism provides the energy and the necessary molecular motions to facilitate the process.

Hormons are produced by special cells, and they are responsible for the communication between various part of the body. Some complicate harmon actions regulates the rate of transport and balance the ion concentrations depending on the portion of the tissue and the need. This is generally called the **hormonal effects** following the suggestion of *human biochemistry*.

Gibbs-Donnan effect considers the equilibrium in compartments that are separated by memberances or cell walls. There will be no net change when the products of concentrations of say $[Na^+]_1$, $[Cl^-]_1$ are the same for compartments 1 and 2.

$$[Na+]1\ [Cl-]1 = [Na+]2\ [Cl-]2$$

the subscript 1 and 2 refer to the two compartments. When no other components are present, we have

$$[Na+]1 = [Cl-]1 = [Na+]2 = [Cl-]2$$

But if compartment 2 has a sodium salt with other anions, this salt ionize to give Na^+ too. The above condition will not be maintained, in this case. In other words, thermodynamic will be a force to adjust the concentrations.

In general, the cations should be balanced with anions. Otherwise, the solution will be charged.

Water in Human Biology

In human, water in the tissue and body fluid is mostly free, but some fraction may be bounded in pockets of hydrophilic compartments. Body fluids have many electrolytes and neutrients dissolve in them.

Intracellular fluid	70%
Interstitial fluid (lymph)	20%
Blood plasma	7%
Intestinal lumen etc.	3%

Human Biochemistry by J.M. Orten and O.W. Neuhaus (1982), 10th Ed. suggests that about 70% of human body weight is water, most found in three major compartments: 70% intracellular fluid, 20% interstitial fluid, and 7% blood plasma, and only 3 % in intestinal lumen, cerebrospinal fluid and other compartments.

However, *Human Biochemistry* also suggests that blood makes up about 8% of the total body weight.

Example 1

For a person weighing 50 kg (110 lb), what is the weight of the blood?

Solution
From the distribution given above,

$$\text{Amount of blood} = 50\ \text{kg} * 0.08$$
$$= 4\ \text{kg}.$$

This is a lot of blood, and donating 0.5 L of blood will not affect the normal function of the blood.

Input		Output	
Drinking	400 g	Skin	500 g
Beverage	580	Expired air	350
Preformed water in solid food	720	Urine	1100
Metabolic water	320	Feces	150
Total	2020	**Total**	2100
Balance	-80 g?		

Water in human comes from ingestion. Aside from drinking water, there is other beverages. Much of the food also contain water. When food is oxidized in the cells, all hydrogen in food converts to water, which is called metabolic water. Water is excreted via urine, feces, skin, and expiration. A typical daily water balance is shown in a table here. Water balance is maintained between cells and fluid, and the output depends on kidney functions and body insensible perspiration (Expired air from the lung is saturated with water vapor, and evaporation from the skin).

Drinking Water

Drinking water affects health. An Excite search using the phrase "drinking water" came up with 57890 documents. Drinking Water Resources gives annotated links to web sites that provide information about the drinking water.

A rather recent book *Chemistry of Water Treatment* by S.D. Faust and O.M. Aly, 2nd Ed. (1998) [TD433 F38 1998] addresses the standards for drinking water in the first Chapter. The standards have changed over the years, as we better understand the science.

Safe drinking water is a suitable combination of minerals and electrolytes. Usually, one should not drink water softened by water softeners. Using distilled water for beverages and cooking may not reach your set goals. Hard water with calcium and magnesium ions is good for drinking.

Usually, a government set up a non-profit organization to provide rules for safe drinking water. This organization has an infrastructure to monitor drinking water systems, and it shall also carry out research to improve the quality of drinking water.

Regarding making rules, reliable tests should be developed to determine the electrolyte we have mentioned, plus others such as lead ions, Pb^{2+}, mercury Hg^{2+}, methylmercury, arsenic, radioactivity, etc. Bacteria tests should be carried out regularly. This organization should also have a communication channel to release relavant message.

The Environmental Protection Agency of the U.S. gives a list of comtaminants. The list has suggested limits, and it divides the contaminants into

- Inorganic substnaces
- Organic substances
- Radioactivities (alpha and beta rays, radium)
- Micro-organisms

Among inorganic substances, limits are given to contents of antimony, arsenic, asbestos, barium, beryllum, cadmium, chromium, copper, mercury, nitrate, nitrite, selenium, and thallium.

More than 50 organic compounds are on the list, and some familar ones are: acrylamide, benzene, carbon tetrachloride, chlorobenzene, 2 4 D, dichlorobenzen, dioxin, polychlorinated biphenyls (PCBs), toluene, and vinyl chloride. Many of these have a zero limit.

In terms of microorganisms, *Giardia lamblia*, and *Legionella*, are checked. Furthermore, viruses, turbidity, total coliforms, and heterotrophic plate should be checked.

Contaminant	Standard
Aluminum	0.05 to 0.2 mg/L
Chloride	250 mg/L
Color	15 (color units)
Copper	1.0 mg/L
Corrosivity	noncorrosive
Fluoride	2.0 mg/L
Foaming Agents	0.5 mg/L
Iron	0.3 mg/L
Manganese	0.05 mg/L
Odor	3 threshold odor number
pH	6.5-8.5
Silver	0.10 mg/L
Sulfate	250 mg/L
Total Dissolved Solids	500 mg/L
Zinc	5 mg/L

The secondary standard lists most electrolytes as shown in this table on the right.

The Secondary Drinking Water Standards are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water.

There are many brands of bottled drinking water, they have been very popular only in recent years. Do we know the bottle procedure? Is the industry regulated? Is the water quality reliable? Are all bottled water the same? Is there a brand bottled water for real good health? Do we know what should be in healthy drinking water? There is an opinion expressed in Ontario Clean Water Agency (OCWA). Check it out.

The magnesium web site gave the following news release Oct. 4, 1999. *According to the U.S. National Academy of Sciences (1977) there have been more than 50 studies, in nine countries, that have indicated an inverse relationship between water hardness and mortality from cardiovascular disease. That is, people who drink water that is deficient in magnesium and calcium generally appear more susceptible to this disease. The U.S. National Academy of Sciences has estimated that a nation-wide initiative to add calcium and magnesium to soft water might reduce the annual cardiovascular death rate by 150,000 in the United States.* This is a good summary from the report.

Sports Drinks

Sports talk gives information about Sports Drinks. This is science, art, testing, and myth. However, some fundamentals should be considered.

Our bodies are mostly water, about 70%. The body fluid has many different things dissolved in it, particularly salt. the salinity -

varies somewhat with where you take the sample of water to measure. Don't worry about that). I recall the concentration as being 0.5%, but I'm not sure. Doctors call this "normal saline".

Now if you put a human, or other animal, cell in saltwater that is the same concentration as the saltwater inside the cell, the cell pretty much just sits there. If you put it in distilled water, the cell absorbs the water through its cell membrane - called diffusion - until it eventually pops. If you put the cell in concentrated saltwater, the cell looses water. The water diffuses out of the cell through the membrane, leaving a small, shriveled up cell.

What does this have to do with sports drinks? If you give someone distilled water, it seems like they would absorb the water faster because of what I just described. On the other hand, during sweating, you're loosing sodium, potassium and small quantities of other electrolytes. If you're exercising particularly long or hard, you need to replace those electrolytes. Researchers found that adding some salt to water replaced the salt lost through sweating and helped the body to get water to the cells. If you look at a label on a Gatorade or other drink, you'll find that the main electrolyte is simple salt. But if you put too much of the electrolytes in the water, the cells shrivel up just like the way I described above.

I hope that helps you understand what happens. This stuff on how cells swell up or shrivel up is in high school biology books, and maybe even in something you can find in your school's library.

Taste and Order of Drinks

Taste and order are sensations, and thus hard to quantify and systematize. Often, the Weber Fechner law is used. This law expresses the taste or order sensations S as being proportional to the logarithm of the stimulus *R*, with the proportional constant *K*,

$$S = K \log R$$

For some common substances, the minimum amounts detected by *expert nose* or *expert taster* gives the sensation as a threshold, below which no taste or order was detected.

However, orderous sensation of water may be reported as threshold order number (TON). If *A* mL of ordorous sample is diluted with *B* mL of order-free water to be "just detectable" to the *expert nose*, the TON is defined as

$$TON = \frac{A + B}{A}$$

Similarly, a flavour threshold number (FTN) can be defined in the same manner.

$$FTN = \frac{A + B}{A}$$

except that *A* and *B* are volumes of samples and taste free water used.

These formulations show a method of defining some quantities that are, otherwise, very diffcult to quantify. There are other methods of reporting orders and taste, and some bottling companies have their standard methods of comparison.

Of course, the source of order and taste comes are organic, inorganic compounds as well as bacteria, algae. For example, mercaptans such as C_2H_2SH and ammonia offers disagreeable smell and taste.

Example 2

A sample of water was tested by 10 expert noses, and only 5 of them can detect an order. Thus, this is "just detected". What is the TON for this sample?

Solution

Since no dilution was used,

$$TON = A / A = 1.$$

DISCUSSION

If equal amount of orderless water is required to dilute it so that the order is "just detected", then the test order number is (1+1)/1 = 2.

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18.7: Green Chemistry

Green chemistry, also called sustainable chemistry, is an area of chemistry and chemical engineering focused on the design of products and processes that minimize the use and generation of hazardous substances. Whereas environmental chemistry focuses on the effects of polluting chemicals on nature, green chemistry focuses on technological approaches to preventing pollution and reducing consumption of nonrenewable resources.

Green chemistry overlaps with all subdisciplines of chemistry but with a particular focus on chemical synthesis, process chemistry, and chemical engineering, in industrial applications. To a lesser extent, the principles of green chemistry also affect laboratory practices. The overarching goals of green chemistry—namely, more resource-efficient and inherently safer design of molecules, materials, products, and processes—can be pursued in a wide range of contexts.

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18.E: Chemistry of the Environment (Exercises)

18.E: Chemistry of the Environment (Exercises)

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19: CHEMICAL THERMODYNAMICS

Our goal in this chapter is to extend the concepts of thermochemistry to an exploration of thermodynamics (from the Greek *thermo* and *dynamic*, meaning “heat” and “power,” respectively), the study of the interrelationships among heat, work, and the energy content of a system at equilibrium. Thermodynamics tells chemists whether a particular reaction is energetically possible in the direction in which it is written, and it gives the composition of the reaction system at equilibrium. It does not, however, say anything about whether an energetically feasible reaction will *actually* occur as written, and it tells us nothing about the reaction rate or the pathway by which it will occur (described by chemical kinetics). Chemical thermodynamics provides a bridge between the macroscopic properties of a substance and the individual properties of its constituent molecules and atoms. As you will see, thermodynamics explains why graphite can be converted to diamond; how chemical energy stored in molecules can be used to perform work; and why certain processes, such as iron rusting and organisms aging and dying, proceed spontaneously in only one direction, requiring no net input of energy to occur.

19.1: Spontaneous Processes

19.2: Entropy and the Second Law of Thermodynamics

19.3: The Molecular Interpretation of Entropy

19.4: Entropy Changes in Chemical Reactions

19.5: Gibbs Free Energy

19.6: Free Energy and Temperature

19.7: Free Energy and the Equilibrium Constant

19.E: Chemical Thermodynamics (Exercises)

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19.1: Spontaneous Processes

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure 19.1.1).

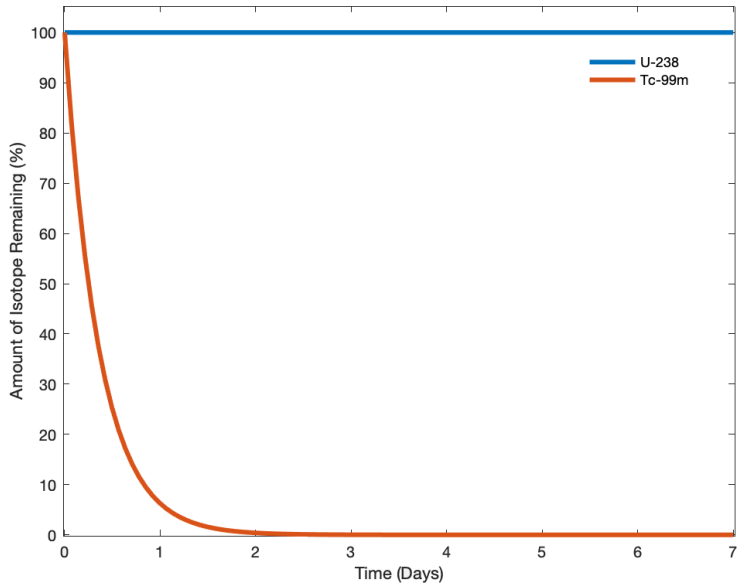


Figure 19.1.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure 19.1.2).

$$\mathrm{C\,(s,\,diamond)} \longrightarrow \mathrm{C\,(s,\,graphite)} \tag{19.1.1}$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow, and so for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

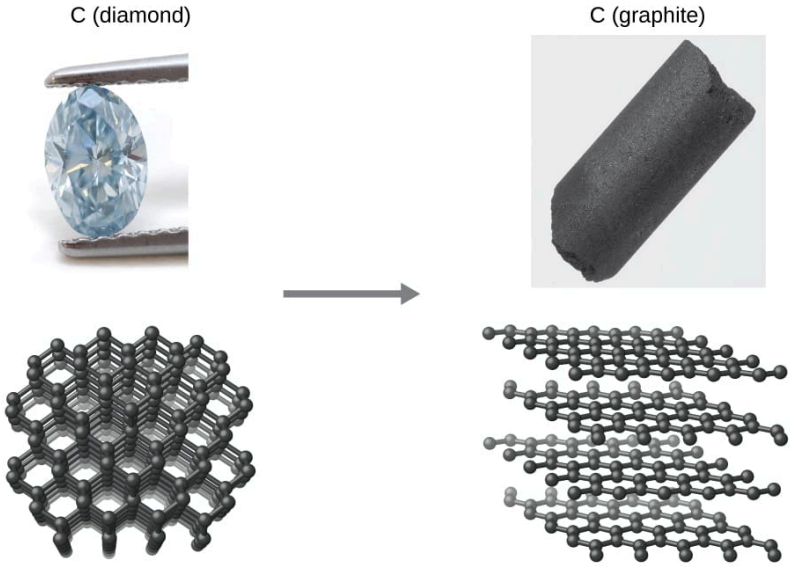


Figure 19.1.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure 19.1.3). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V \tag{19.1.2}$$

$$= 0 \;\; (\mathrm{P} = 0 \text{ in a vaccum}) \tag{19.1.3}$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The first law of thermodynamics confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w \qquad \text{(First Law of Thermodynamics)}$$

$$= 0 + 0 = 0 \tag{19.1.4}$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas appears to be related to the greater, more *uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more

uniformly (present in equal amounts in each flask).

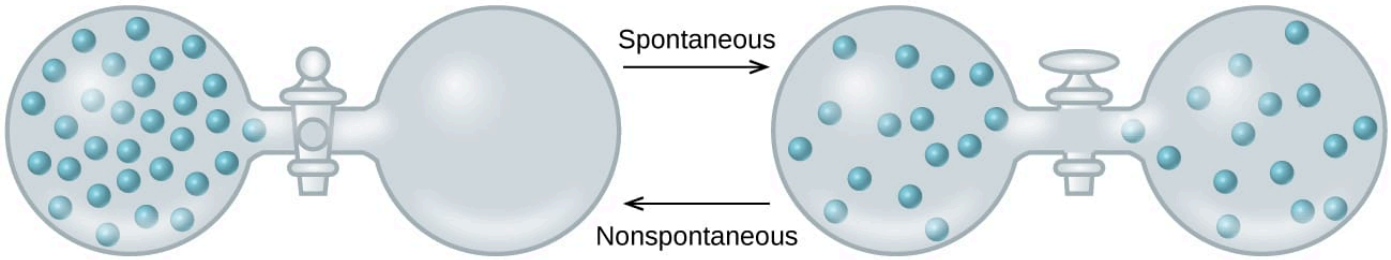


Figure 19.1.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

When the valve is closed, all of the gas molecules accumlating only in one side of the flask. The diagram with the open valve shows gas being equally distributed among the two flasks. The dispersion of the gas is labeled as spontaneous while the reverse is labeled as non spontaneous.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 19.1.4). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \tag{19.1.5}$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure 19.1.4:When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 19.1.1: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution



Figure 19.1.5:(credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Sahar Atwa)

This figure has three photos labeled, “a,” “b,” and “c.” Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

a. *Sublimation* is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
b. *Condensation* is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

Exercise 19.1.1

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer available at the end of this section.

Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process
: process that requires continual input of energy from an external source

spontaneous change
: process that takes place without a continuous input of energy from an external source

Answers

Exercise 19.1.1

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

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19.2: Entropy and the Second Law of Thermodynamics

Learning Objectives

- To understand the relationship between internal energy and entropy.

The first law of thermodynamics governs changes in the state function we have called internal energy (U). Changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned previously that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure 19.2.1.

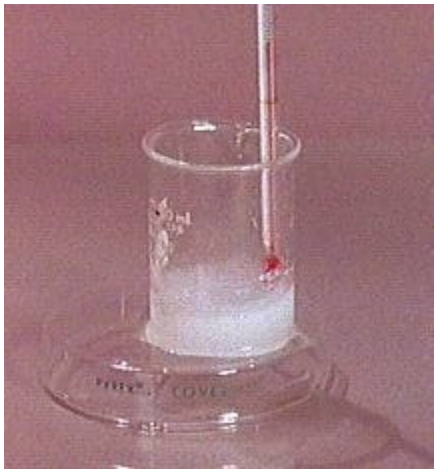


Figure 19.2.1: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously

come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called **entropy (S)**, a thermodynamic property of all substances that is proportional to their degree of "disorder". In Chapter 13, we introduced the concept of entropy in relation to solution formation. Here we further explore the nature of this state function and define it mathematically.

Entropy

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states: $\Delta S = S_f - S_i$.

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or microstates, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

We can illustrate the concepts of microstates and entropy using a deck of playing cards, as shown in Figure 19.2.2. In any new deck, the 52 cards are arranged by four suits, with each suit arranged in descending order. If the cards are shuffled, however, there are approximately 10^{68} different ways they might be arranged, which corresponds to 10^{68} different microscopic states. The entropy of an ordered new deck of cards is therefore low, whereas the entropy of a randomly shuffled deck is high. Card games assign a higher value to a hand that has a low degree of disorder. In games such as five-card poker, only 4 of the 2,598,960 different possible hands, or microstates, contain the highly ordered and valued arrangement of cards called a royal flush, almost 1.1 million hands contain one pair, and more than 1.3 million hands are completely disordered and therefore have no value. Because the last two arrangements are far more probable than the first, the value of a poker hand is inversely proportional to its entropy.

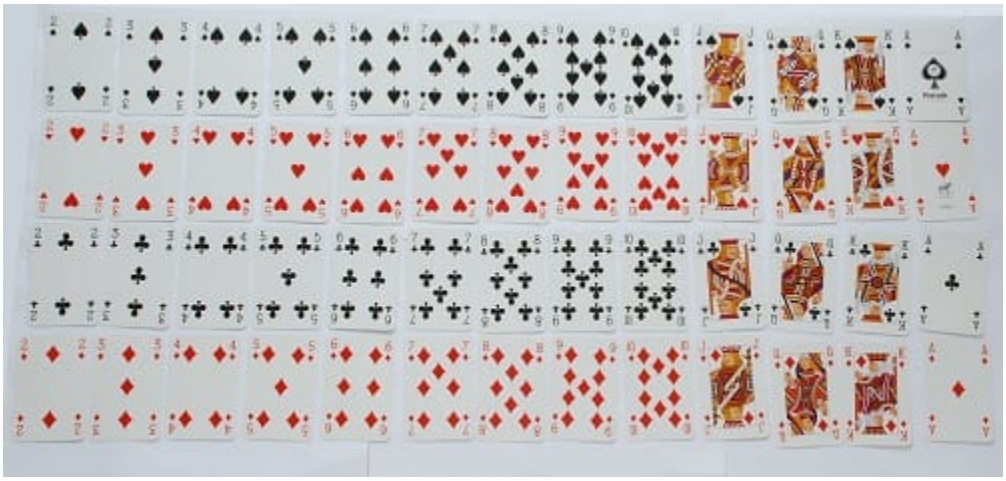


Figure 19.2.2: Illustrating Low- and High-Entropy States with a Deck of Playing Cards. An new, unshuffled deck has only a single arrangement, so there is only one microstate. In contrast, a randomly shuffled deck can have any one of approximately 10^{68} different arrangements, which correspond to 10^{68} different microstates. (CC BY-3.0 ; Trainler).

We can see how to calculate these kinds of probabilities for a chemical system by considering the possible arrangements of a sample of four gas molecules in a two-bulb container (Figure 19.2.3). There are five possible arrangements: all four molecules in the left bulb (I); three molecules in the left bulb and one in the right bulb (II); two molecules in each bulb (III); one molecule in the left bulb and three molecules in the right bulb (IV); and four molecules in the right bulb (V). If we assign a different color to each molecule to keep track of it for this discussion (remember, however, that in reality the molecules are indistinguishable from one another), we can see that there are 16 different ways the four molecules can be distributed in the bulbs, each corresponding to a particular microstate. As shown in Figure 19.2.3, arrangement I is associated with a single microstate, as is arrangement V, so each arrangement has a probability of 1/16. Arrangements II and IV each have a probability of 4/16 because each can exist in four microstates. Similarly, six different microstates can occur as arrangement III, making the probability of this arrangement 6/16. Thus the arrangement that we would expect to encounter, with half the gas molecules in each bulb, is the most probable arrangement. The others are not impossible but simply less likely.

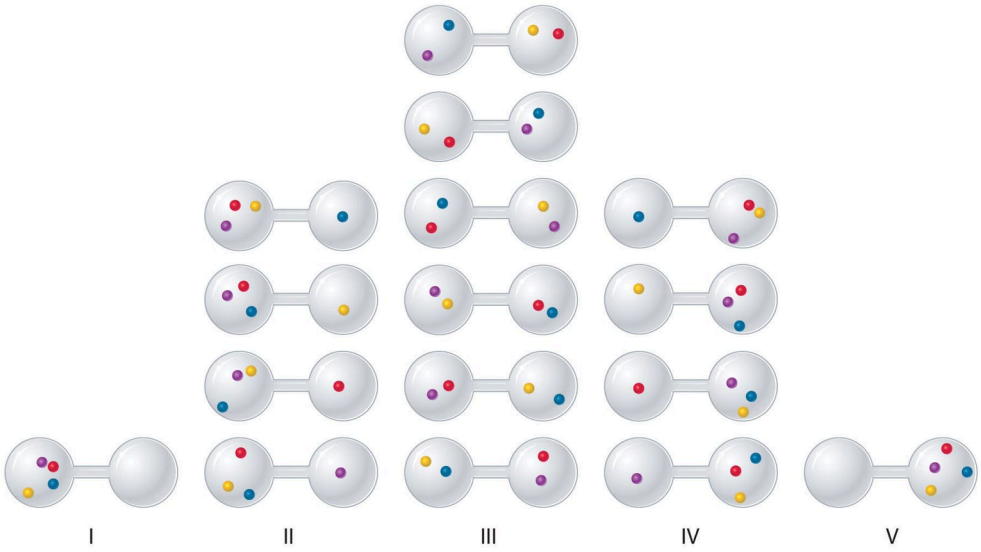


Figure 19.2.3: The Possible Microstates for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume

There are 16 different ways to distribute four gas molecules between the bulbs, with each distribution corresponding to a particular microstate. Arrangements I and V each produce a single microstate with a probability of 1/16. This particular arrangement is so improbable that it is likely not observed. Arrangements II and IV each produce four microstates, with a probability of 4/16. Arrangement III, with half the gas molecules in each bulb, has a probability of 6/16. It is the one encompassing the most microstates, so it is the most probable.

Instead of four molecules of gas, let's now consider 1 L of an ideal gas at standard temperature and pressure (STP), which contains 2.69×10^{22} molecules (6.022×10^{23} molecules/22.4 L). If we allow the sample of gas to expand into a second 1 L container, the probability of finding all 2.69×10^{22} molecules in one container and none in the other at any given time is extremely small, approximately $\frac{2}{2.69 \times 10^{22}}$. The probability of such an occurrence is effectively zero. Although nothing prevents the molecules in the gas sample from occupying only one of the two bulbs, that particular arrangement is so improbable that it is never actually observed. The probability of arrangements with essentially equal numbers of molecules in each bulb is quite high, however, because there are many equivalent microstates in which the molecules are distributed equally. Hence a macroscopic sample of a gas occupies all of the space available to it, simply because this is the most probable arrangement.

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

> Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure 19.2.4, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of NaCl and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved Na^+ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the Cl^- ions

also cause the water to adopt a particular local structure. Both of these effects increase the order of the system, leading to a decrease in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors. In the case of an NaCl solution, disruption of the crystalline NaCl structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

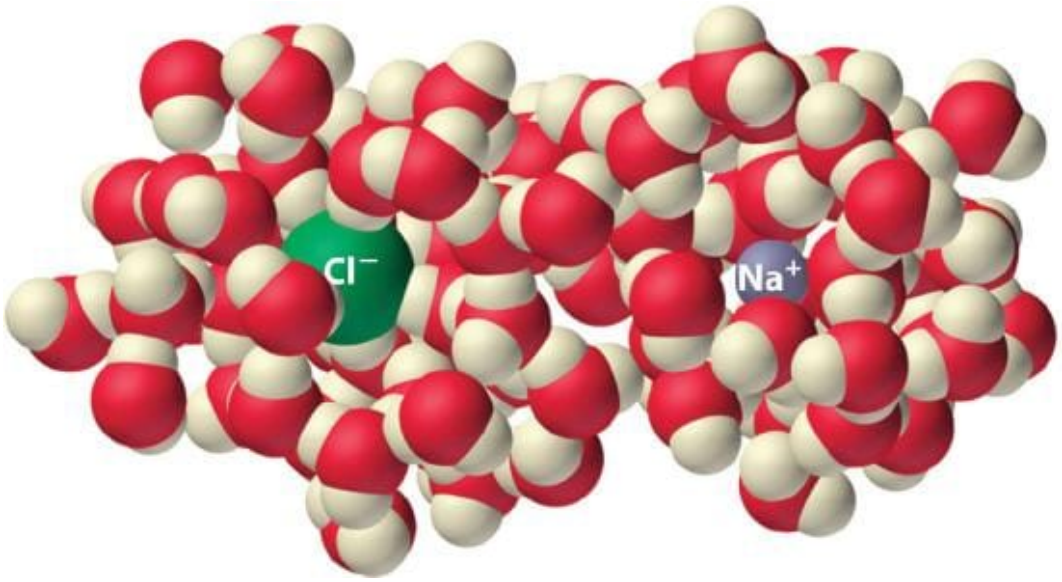


Figure 19.2.4: The Effect of Solution Formation on Entropy

Dissolving NaCl in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

Example 19.2.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.

b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

Exercise 19.2.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of H_2(g) and 1 mol of N_2(g) at 25°C and 1 atm or a sample of 2 mol of NH_3(g) at 25°C and 1 atm

Answer a available at the end of this section.

Video Solution

Reversible and Irreversible Changes

Changes in entropy (ΔS), together with changes in enthalpy (ΔH), enable us to predict in which direction a chemical or physical change will occur spontaneously. Before discussing how to do so, however, we must understand the difference between a reversible process and an irreversible one. In a reversible process, every intermediate state between the extremes is an equilibrium state, regardless of the direction of the change. In contrast, an irreversible process is one in which the intermediate states are not equilibrium states, so change occurs spontaneously in only one direction. As a result, a reversible process can change direction at any time, whereas an irreversible process cannot. When a gas expands reversibly against an external pressure such as a piston, for example, the expansion can be reversed at any time by reversing the motion of the piston; once the gas is compressed, it can be allowed to expand again, and the process can continue indefinitely. In contrast, the expansion of a gas into a vacuum (P_{ext} = 0) is irreversible because the external pressure is measurably less than the internal pressure of the gas. No equilibrium states exist, and the gas expands irreversibly. When gas escapes from a microscopic hole in a balloon into a vacuum, for example, the process is irreversible; the direction of airflow cannot change.

Because work done during the expansion of a gas depends on the opposing external pressure ($w = -P_{ext}\Delta V$), work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, $\Delta U = q + w$. Because U is a state function, the magnitude of ΔU does not depend on reversibility and is independent of the path taken. So

$$\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev} \tag{19.2.1}$$

Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$.

In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{\text{rev}} = T\Delta S \quad \text{and} \quad \Delta S = \frac{q_{\text{rev}}}{T} \tag{19.2.2}$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is $w_{rev} = -P\Delta V$, we can express Equation 19.2.1 as follows:

$$\Delta U = q_{rev} + w_{rev} \tag{19.2.3}$$
$$= T\Delta S - P\Delta V \tag{19.2.4}$$

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the PV work done.

To illustrate the use of Equation 19.2.2 and Equation 19.2.4, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 19.2.5). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta U = 0$ and $q_{rev} = -w_{rev}$. During expansion, ΔV > 0, so the gas performs work on its surroundings:

$$w_{rev} = -P\Delta V < 0.$$

According to Equation 19.2.4, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the system is therefore $\Delta S_{sys} = +q_{rev}/T$, and the entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{q_{rev}}{T}.$$

The corresponding change in entropy of the universe is then as follows:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= \frac{q_{\text{rev}}}{T} + \left(-\frac{q_{\text{rev}}}{T}\right) \\ &= 0\end{aligned}$$

Thus no change in ΔS_{univ} has occurred.

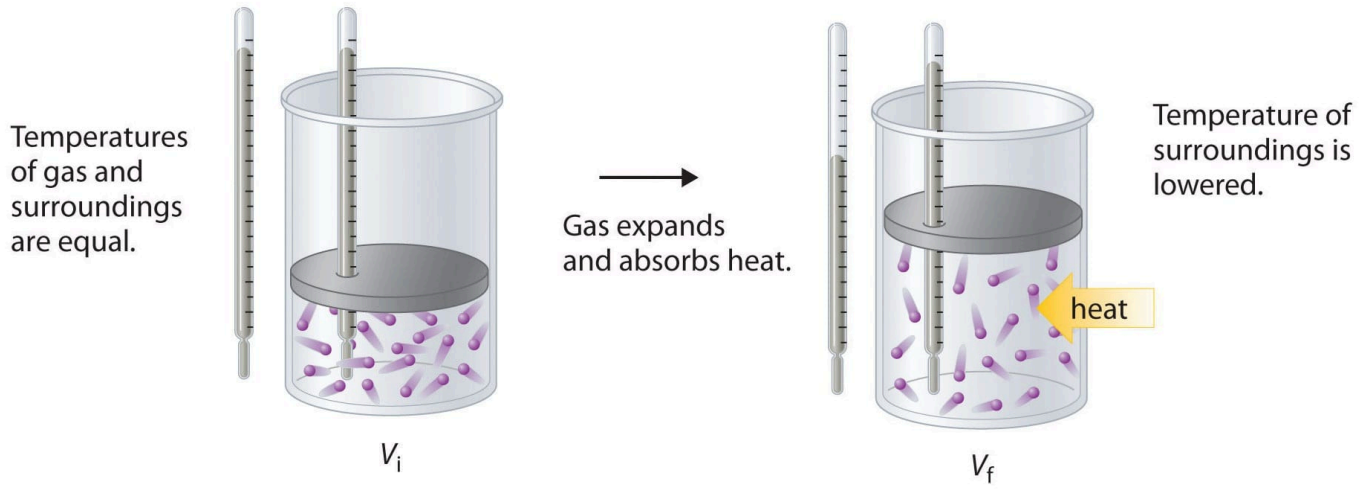


Figure 19.2.5: Expansion of Gas at Constant Temperature

Temperatures of gas and surroundings are equal. Then the gas expands and absorbs heat. Temperature of the surroundings is then lowered.

In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 19.2.6. The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 19.2.2, we see that the entropy of fusion of ice can be written as follows:

$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fus}}}{T}$$

By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.

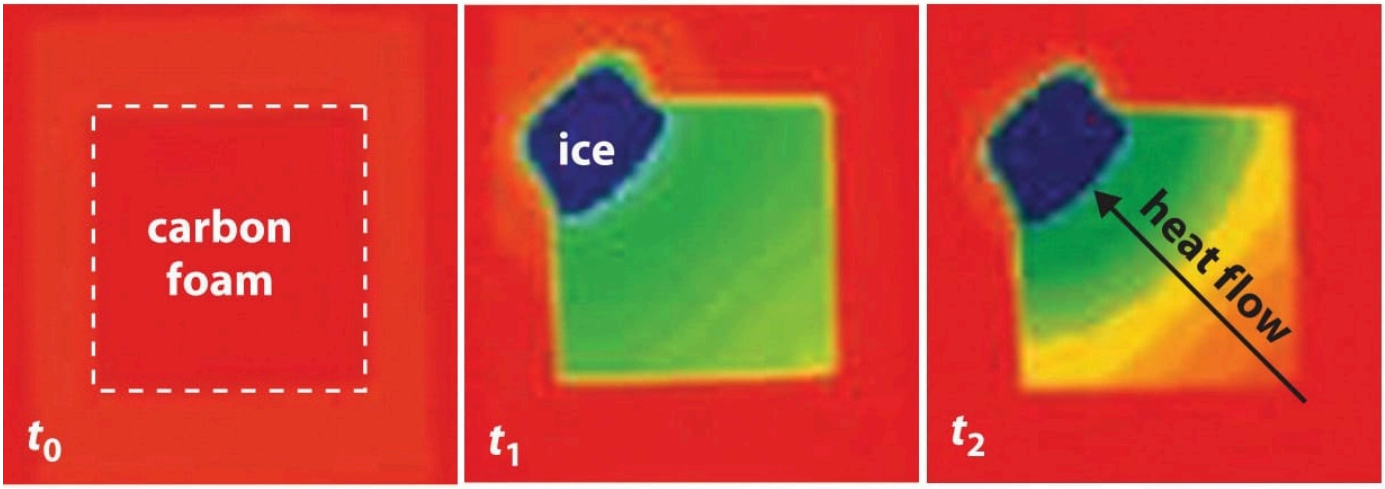


Figure 19.2.6: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

In this case, ΔS_{fus} = (6.01 kJ/mol)/(273 K) = 22.0 J/(mol•K) = ΔS_{sys}. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so $\Delta S_{surr} = q_{rev}/T$ = –(6.01 kJ/mol)/(273 K) = –22.0 J/(mol•K). Once again, we see that the entropy of the universe does not change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 22.0 \text{ J/(mol•K)} - 22.0 \text{ J/(mol•K)} = 0$$

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of the second law of thermodynamics: the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process.

The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an observable non-spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{\text{univ}} = \Delta S_{\text{cold}} + \Delta S_{\text{hot}} = \frac{q}{T_{\text{cold}}} + \left(-\frac{q}{T_{\text{hot}}}\right) \tag{19.2.5}$$

The numerators on the right side of Equation 19.2.5 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as

written. Conversely, any process for which ΔS_{univ} is negative will not occur as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 19.2.7).



Figure 19.2.7: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

Example 19.2.2: Tin Pest

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon was argued to have plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers' uniforms were made of tin and may have disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with ΔH = –2.1 kJ/mol at 13.2°C.

a. What is ΔS for this process?
b. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 19.2.2 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution

a. We know from Equation 19.2.2 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where q_{rev} = ΔH. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{(-2.1\ \text{kJ/mol})(1000\ \text{J/kJ})}{286.4\ \text{K}} = -7.3\ \ \text{J/(mol} \cdot \text{K)}$$

b. The fact that $\Delta S < 0$ means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.

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Video 19.2.1**:** *Time lapse tin pest reaction.*

Note: Whether failing buttons were indeed a contributing factor in the failure of the invasion remains disputed; critics of the theory point out that the tin used would have been quite impure and thus more tolerant of low temperatures. Laboratory tests provide evidence that the time required for unalloyed tin to develop significant tin pest damage at lowered temperatures is about 18 months, which is more than twice the length of Napoleon's Russian campaign. It is clear though that some of the regiments employed in the campaign had tin buttons and that the temperature reached sufficiently low values (at least -40 °C)

Exercise 19.2.2

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with $\Delta H = 0.401$ kJ/mol at 1 atm.

a. What is ΔS for this process?
b. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer a available at the end of this section.

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Summary

For a given system, the greater the number of microstates, the higher the entropy. During a spontaneous process, the entropy of the universe increases.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

A measure of the disorder of a system is its entropy (S), a state function whose value increases with an increase in the number of available microstates. A reversible process is one for which all intermediate states between extremes are equilibrium states; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

Answers

Exercise 19.2.1

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

a mixture of 3 mol of H_2(g) and 1 mol of N_2(g) at 25°C and 1 atm (more molecules of gas are present)

Exercise 19.2.2

1.09 J/(mol•K)

S_α

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19.3: The Molecular Interpretation of Entropy

Learning Objectives

- To understand entropy from a molecular interpretation

As discussed previously, the second law of thermodynamics argues that all processes **must** increase the total entropy of the universe. However, the universe if often separated into the System and the Surroundings differing changes of entropy can be observed from a system level perspective. Many processes results in an increase in a *system*'s entropy $\Delta S > 0$:

- Increasing the volume that a gas can occupy will increase the disorder of a gas
- Dissolving a solute into a solution will increase the entropy of the solute - typically resulting in an increase in the entropy of the system. (Note: the solvation of a solute can sometimes result in a significant *decrease* in the *solvent* entropy - leading to a *net decrease* in entropy of the *system*)
- Phase changes from solid to liquid, or liquid to gas, lead to an increase in the entropy of the system

Some processes result in a *decrease* in the entropy of a *system* $\Delta S < 0$:

- A gas molecule dissolved in a liquid is much more confined by neighboring molecules than when its in the gaseous state. Thus, the entropy of the gas molecule will decrease when it is dissolved in a liquid
- A phase change from a liquid to a solid (i.e. freezing), or from a gas to a liquid (i.e. condensation) results in an *decrease in the disorder* of the substance, and a *decrease in the entropy*
- A chemical reaction between gas molecules that results in *a net decrease* in the overall **number** of gas molecules will de*crease the disorder* of the system, and result in a *decrease in the entropy*

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)} \quad \Delta S < 0 \tag{19.3.1}$$

What is the molecular basis for the above observations for the change in entropy? Let's first consider the last example, the decrease in entropy associated with a decrease in the number of gas molecules for a chemical reaction

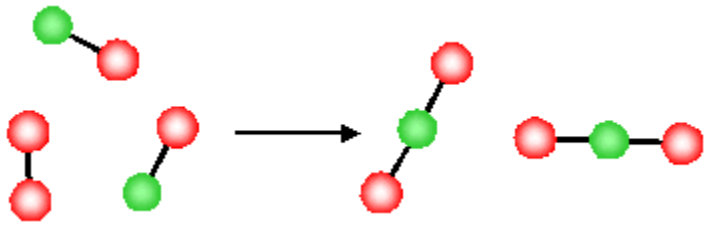


Figure 19.3.1: $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

The product of this reaction (NO_2) involves *the formation of a new N-O bond* and the O atoms, originally in a separate O_2 molecule, *are now connected* to the NO molecule via a new $N - O$ bond.

- Since they are now physically bonded to the other molecule (forming a new, larger, single molecule) the O atoms have *less freedom* to move around
- The reaction has resulted in a loss of freedom of the atoms (O atoms)
- There is a reduction in the disorder of the system (i.e. due to the reduction in the degrees of freedom, the system is *more ordered* after the reaction). $\Delta S < 0$.

Molecular Degrees of Freedom

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 19.3.2).

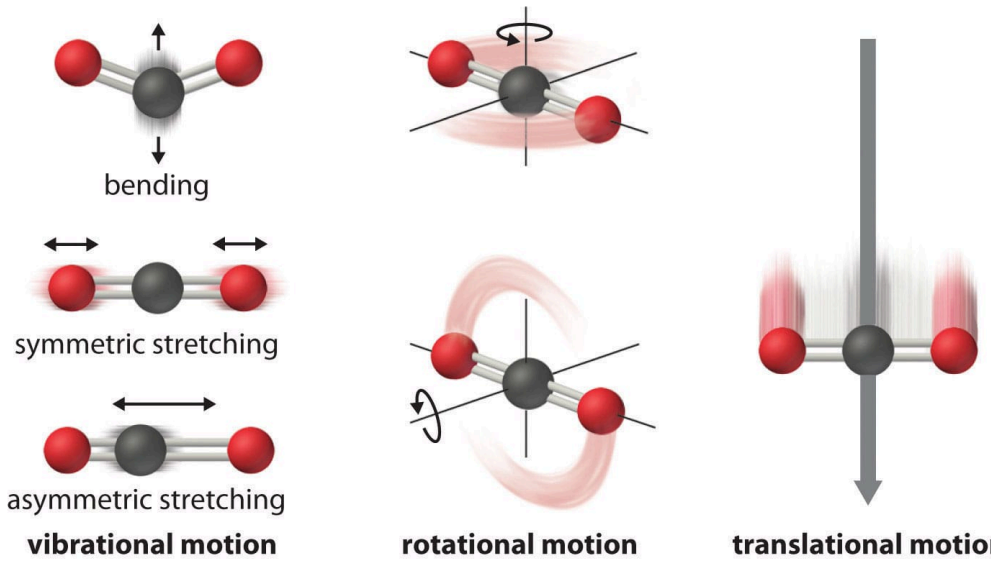


Figure 19.3.2: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

- *Translational motion*. The entire molecule can move in some direction in three dimensions
- *Rotational motion*. The entire molecule can rotate around any axis, (even though it *may not actually change its position translationally*)
- *Vibrational motion*. The atoms within a molecule have certain freedom of movement relative to each other; this displacement can be periodic motion like the vibration of a tuning fork

These forms of molecular motion are ways in which molecules can store energy. The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy.

The Third Law of Thermodynamics

These forms of motion are ways in which the molecule can store energy. The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum effects). Such a state of perfect order (or, conversely, zero disorder) corresponds to zero entropy. In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the *third law of thermodynamics*: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

The Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute zero (i.e. 0 Kelvin) is 0.

Since S = 0 corresponds to *perfect order*. The position of the atoms or molecules in the crystal would be perfectly defined

- As the temperature increases, the entropy of the atoms in the lattice increase
- Vibrational motions cause the atoms and molecules in the lattice to be less well ordered

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature.In practice, chemists determine the absolute entropy of a substance by measuring

the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

Motion never stops at absolute zero!

From classical kinetic theory, all motions cease at absolute zero. However things are more complicated from the more advanced (and more accurate) quantum mechanics. The Heisenberg Uncertainly Principle of quantum mechanics argues that molecules, even at absolute zero, always always have motion. Nonetheless, this motion is often ignored in the introduction of the third law of thermodynamics (which is incorrect of course).

Continued heating of a Solid Lattice

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy (S°), which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of S° are J/(mol·K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K [corresponding to S = 0 J/(mol·K)] and 298 K.

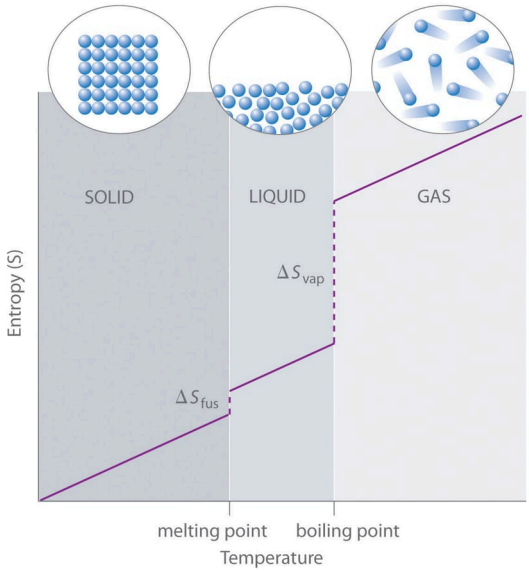


Figure 19.3.3: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}).

As shown in Table 19.3.1, for substances with approximately the same molar mass and number of atoms, S° values fall in the order S°(gas) > S°(liquid) > S°(solid). For instance, S° for liquid water is 70.0 J/(mol·K), whereas S° for water vapor is 188.8 J/(mol·K). Likewise, S° is 260.7 J/(mol·K) for gaseous I_2 and 116.1 J/(mol·K) for solid I2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases. The correlation between physical state and absolute entropy is illustrated in Figure 19.3.2, which is a generalized plot of the entropy of a substance versus temperature.

Table 19.3.1: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		Liquids		Solids	
Substance	*S° [J/(mol·K)]*	*Substance*	*S° [J/(mol·K)]*	*Substance*	*S° [J/(mol·K)]*

Gases		Liquids		Solids	
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.

A closer examination of Table 19.3.1 also reveals that substances with similar molecular structures tend to have similar S° values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond [S° = 2.4 J/(mol·K)]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S° [5.7 J/(mol·K)] due to more disorder in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S° values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S°, which reflects a more ordered structure.

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Summary

In general, the entropy is expected to *increase* for the following types of processes:

1. The melting of a solid to form a liquid
2. The vaporization of a liquid (or solid) to produce a gas
3. Chemical reactions that involve phase changes of $\text{solid} \rightarrow \text{liquid/gas}$, or $\text{liquid} \rightarrow \text{gas}$
4. Chemical reactions that result in an increase in the number of gaseous molecules
5. Any time the temperature of a substance is increased

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19.4: Entropy Changes in Chemical Reactions

Learning Objectives

- To calculate entropy changes for a chemical reaction

We have seen that the energy given off (or absorbed) by a reaction, and monitored by noting the change in temperature of the surroundings, can be used to determine the enthalpy of a reaction (e.g. by using a calorimeter). Tragically, there is no comparable easy way to experimentally measure the change in entropy for a reaction. Suppose we know that energy is going into a system (or coming out of it), and yet we do not observe any change in temperature. What is going on in such a situation? Changes in internal energy, that are not accompanied by a temperature change, might reflect changes in the entropy of the system.

For example, consider water at °0C at 1 atm pressure

- This is the temperature and pressure condition where liquid and solid phases of water are in equilibrium (also known as the melting point of ice)

$$\mathrm{H_2O\,(s)} \rightarrow \mathrm{H_2O\,(l)} \tag{19.4.1}$$

- At such a temperature and pressure we have a situation (by definition) where we have some ice and some liquid water
- If a small amount of energy is input into the system the equilibrium will shift slightly to the right (i.e. in favor of the liquid state)
- Likewise if a small amount of energy is withdrawn from the system, the equilibrium will shift to the left (more ice)

> However, in both of the above situations, the energy change is not accompanied by a change in temperature (the temperature will not change until we no longer have an equilibrium condition; i.e. all the ice has melted or all the liquid has frozen)

Since the quantitative term that relates the amount of heat energy input vs. the rise in temperature is the heat capacity, it would seem that in some way, information about the heat capacity (and how it changes with temperature) would allow us to determine the entropy change in a system. In fact, values for the "standard molar entropy" of a substance have units of J/mol K, the same units as for molar heat capacity.

Standard Molar Entropy, S^0

The entropy of a substance has an absolute value of 0 entropy at 0 K.

- **Standard molar entropies** are listed for a reference temperature (like 298 K) and 1 atm pressure (i.e. the entropy of a pure substance at 298 K and 1 atm pressure). A table of standard molar entropies at 0K would be pretty useless because it would be 0 for every substance (duh!) Standard molar entropy values are listed for a variety of substances in Table T2.
- When comparing standard molar entropies for a substance that is either a solid, liquid or gas at 298 K and 1 atm pressure, the gas will have more entropy than the liquid, and the liquid will have more entropy than the solid
- Unlike *enthalpies of formation*, standard molar entropies of elements are not 0.

The entropy change in a chemical reaction is given by the sum of the entropies of the products minus the sum of the entropies of the reactants. As with other calculations related to balanced equations, the coefficients of each component must be taken into account in the entropy calculation (the *n*, and *m*, terms below are there to indicate that the coefficients must be accounted for):

$$\Delta S^0 = \sum_n nS^0(products) - \sum_m mS^0(reactants)$$

Example 19.4.1: Haber Process

Calculate the change in entropy associated with the Haber process for the production of ammonia from nitrogen and hydrogen gas.

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)} \rightleftharpoons \mathrm{2\,NH_3\,(g)}$$

At 298K as a standard temperature:

- $S^0(NH_3)$ = 192.5 J/mol K
- $S^0(H_2)$ = 130.6 J/mol K
- $S^0(N_2)$ = 191.5 J/mol K

Solution

From the balanced equation we can write the equation for ΔS^0 (the change in the standard molar entropy for the reaction):

$$\Delta S^0 = 2*S^0(NH_3) - [S^0(N_2) + (3*S^0(H_2))]$$

$$\Delta S^0 = 2*192.5 - [191.5 + (3*130.6)]$$

$$\Delta S^0 = -198.3 \text{ J/mol K}$$

It would appear that the process results in a ***decrease*** in entropy - i.e. a decrease in disorder. This is expected because we are decreasing the number of gas molecules. In other words the $N_2(g)$ used to float around independently of the H_2 gas molecules. After the reaction, the two are bonded together and can't float around freely from one another. (I guess you can consider marriage as a negative entropy process!)

To calculate ΔS° for a chemical reaction from standard molar entropies, we use the familiar “products minus reactants” rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 19.4.2 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

> ΔS° for a reaction can be calculated from absolute entropy values using the same “products minus reactants” rule used to calculate ΔH°.

Example 19.4.2: Combustion of Octane

Use the data in Table T2 to calculate ΔS° for the combustion reaction of liquid isooctane with O_2(g) to give CO_2(g) and H_2O(g) at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table T2. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS° for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \rightarrow 8\,CO_2\,(g) + 9\,H_2O\,(g)$$

We calculate ΔS° for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{aligned}\Delta S^\circ_{rxn} &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})\\ &= [8S^\circ(CO_2) + 9S^\circ(H_2O)] - [S^\circ(C_8H_{18}) + \frac{25}{2}S^\circ(O_2)]\\ &= \{[8\text{ mol } CO_2 \times 213.8\text{ J/(mol}\cdot\text{K)}] + [9\text{ mol } H_2O \times 188.8\text{ J/(mol}\cdot\text{K)}]\}\\ &\quad - \left\{[1\text{ mol } C_8H_{18} \times 329.3\text{ J/(mol}\cdot\text{K)}] + \left[\frac{25}{2}\text{ mol } O_2 \times 205.2\text{ J/(mol}\cdot\text{K)}\right]\right\}\\ &= 515.3\text{ J/K}\end{aligned}$$

ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise 19.4.2

Use the data in Table T2 to calculate ΔS° for the reaction of H_2(g) with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer available at the end of this section.

YouTube Video

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Answers

Exercise 19.4.2

–361.1 J/K

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19.5: Gibbs Free Energy

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for both a system and its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy (G), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{19.5.1}$$

Because it is a combination of state functions, G is also a state function.

J. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled “On the Equilibrium of Heterogeneous Substances” was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{19.5.2}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 19.5.2 to $\Delta G = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{19.5.3}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \tag{19.5.4}$$

$$= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \tag{19.5.5}$$

Multiplying both sides of the inequality by –T reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0$$

which is equal to ΔG (Equation 19.5.2). We can therefore see that for a spontaneous process, $\Delta G < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 19.5.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 19.5.3), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{40{,}657\ \text{J}}{373.15\ \text{K}} \\ &= 108.96\ \text{J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\text{ J} - [(383.15\text{ K})(108.96\text{ J/K})] \\ &= -1091\text{ J}\end{aligned}$$

At 110°C, $\Delta G < 0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\text{ J} - [(363.15\text{ K})(108.96\text{ J/K})] \\ &= 1088\text{ J}\end{aligned}$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ\text{C}} = 1090\text{ J} = -\Delta G_{90^\circ\text{C}}$, as we would predict.

Relating Enthalpy and Entropy changes under Equilibrium Conditions

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 19.5.2), setting $\Delta G = 0$, and solving for T,

$$0\text{ J} = 40{,}657\text{ J} - T(108.96\text{ J/K})$$
$$T = 373.15\text{ K}$$

Thus $\Delta G = 0$ at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 19.5.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

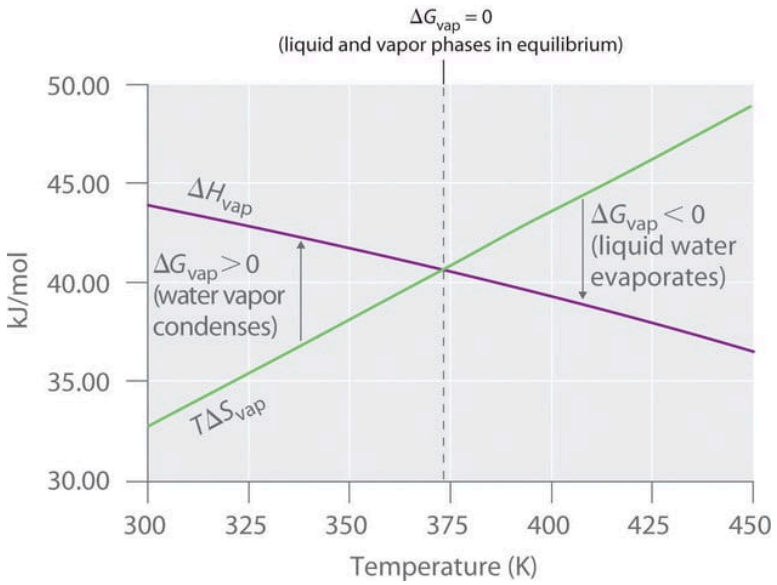


Figure 19.5.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH – TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

Graph of kilojoule per mole against temperature. The purple line is the delta H vaporization. the green line is the T delta S vaporization.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy (ΔH > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid (ΔS > 0). At temperatures greater than 373 K, the TΔS term dominates, and ΔG < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

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The Definition of Gibbs Free Energy: The Definition of Gibbs Free Energy (opens in new window) [youtu.be]

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 19.5.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{19.5.6}$$

This equation tells us that when energy is released during an exothermic process (ΔH < 0), such as during the combustion of a fuel, some of that energy can be used to do work (ΔG < 0), while some is used to increase the entropy of the universe (TΔS > 0). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged.

(For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 19.5.1, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 19.5.1: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach leaf cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10-20
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 19.5.7:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{19.5.7}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG° means that the equilibrium constant is less than 1.

Example 19.5.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O_2\,(l)$$

At 25°C, the standard enthalpy change (ΔH°) is –187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 19.5.7, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG° for the reaction, we need to know ΔH^o, ΔS^o, and T. We are given ΔH^o, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(H_2O_2) - [S^\circ(O_2) + S^\circ(H_2)] \\ &= [1\text{ mol } H_2O_2 \times 109.6\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol } H_2 \times 130.7\text{ J/(mol}\cdot\text{K)}] + [1\text{ mol } O_2 \times 205.2\text{ J/(mol}\cdot\text{K)}]\} \\ &= -226.3\text{ J/K (per mole of } H_2O_2)\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS^o is very negative for this reaction.

B Substituting the appropriate quantities into Equation 19.5.7,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\text{ kJ/mol} - (298.15\text{ K})[-226.3\text{ J/(mol}\cdot\text{K)} \times 1\text{ kJ/1000 J}] \\ &= -187.78\text{ kJ/mol} + 67.47\text{ kJ/mol} \\ &= -120.31\text{ kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS^o and ΔH^o for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH^o and $T\Delta S^o$ terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS^o term and for the energy needed to break bonds in the reactants.

Exercise 19.5.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).$$

Is the reaction spontaneous as written at 25°C?

Hint available at the end of this section.

Answer available at the end of this section.

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Determining if a Reaction is Spontaneous: Determining if a Reaction is Spontaneous(opens in new window) [youtu.be] (opens in new window)

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG_f°)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G_f^\circ = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \tag{19.5.8}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

$$\Delta G_{rxn}^o = \sum m\Delta G_f^o(products) - \sum n\Delta_f^o(reactants) \tag{19.5.9}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

The "Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG°_f values (Table T1) using the “products minus reactants” rule.

Example 19.5.2

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). Use the following data:

- $\Delta G°_f$(isooctane) = −353.2 kJ/mol,
- $\Delta G°_f(CO_2)$ = −394.4 kJ/mol, and
- $\Delta G°_f(H_2O)$ = −237.1 kJ/mol. Is the reaction spontaneous as written?

Given: balanced chemical equation and values of $\Delta G°_f$ for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the “products minus reactants” rule to obtain ΔG°_{rxn}, remembering that $\Delta G°_f$ for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

$$C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \;\rightarrow 8\,CO_2\,(g) + 9\,H_2O\,(l)$$

We are given ΔG°_f values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, $\Delta G^\circ_f\,(O_2)$ is zero. Using the "products minus reactants" rule,

$$\begin{aligned}\Delta G^\circ &= [8\Delta G^\circ_f(CO_2) + 9\Delta G^\circ_f(H_2O)] - \left[1\Delta G^\circ_f(C_8H_{18}) + \frac{25}{2}\Delta G^\circ_f(O_2)\right] \\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\ &\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\ &= -4935.9\text{ kJ (per mol of } C_8H_{18})\end{aligned}$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Exercise 19.5.2

Calculate ΔG° for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer available at the end of this section.

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Calculating Grxn using Gf: Calculating Grxn using Gf(opens in new window) [youtu.be]

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 19.5.3

Calculate (a) ΔG° and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)⇌2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),
- $S°(NH_3)$ = 192.8 J/(mol•K), and
- $\Delta H^\circ_f\ (NH_3)$ = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG° and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 19.5.7 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 19.5.2 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 19.5.7, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ_{rxn} &= 2S^\circ(NH_3) - [S^\circ(N_2) + 3S^\circ(H_2)] \\ &= [2\text{ mol } NH_3 \times 192.8\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol } N_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol } H_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\} \\ &= -198.1\text{ J/K (per mole of } N_2) \end{aligned} \tag{19.5.10}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of $\Delta H^\circ_f\ (NH_3)$ is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{rxn} &= 2\Delta H^\circ_f(NH_3) - [\Delta H^\circ_f(N_2) + 3\Delta H^\circ_f(H_2)] \\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})] \\ &= -91.8\text{ kJ(per mole of } N_2)\end{aligned}$$

B Inserting the appropriate values into Equation 19.5.7

$$\Delta G^\circ_{rxn} = \Delta H^\circ - T\Delta S^\circ = (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) = -32.7\text{ kJ (per mole of } N_2)$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 19.5.2:

$$\begin{aligned}\Delta G_{300°C} &= \Delta H_{300°C} - (573\text{ K})(\Delta S_{300°C}) \\ &= \Delta H^\circ - (573\text{ K})\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) \\ &= 21.7\text{ kJ (per mole of } N_2)\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the $-T\Delta S°$ term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

Exercise 19.5.3

Calculate

a. $\Delta G°$ and
b. $\Delta G_{750°C}$

for the following reaction

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- $\Delta H°_f$(NO_2) = 33.2 kJ/mol, and
- $\Delta H°_f$ (NO) = 91.3 kJ/mol.

Answer a available at the end of this section.

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting ΔG° = 0 in Equation 19.5.7, as illustrated in Example 19.5.4.

Example 19.5.4

As you saw in Example 19.5.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 9.5.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG° equal to zero in Equation 19.5.7 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 19.5.3, we calculated that ΔH° is –91.8 kJ/mol of N_2 and ΔS° is –198.1 J/K per mole of N_2, corresponding to ΔG° = –32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG° equal to zero and rearranging Equation 19.5.7 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{-198.1\ \text{J/K}} = 463\ \text{K}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise 19.5.4

As you found in the exercise in Example 19.5.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer available at the end of this section.

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change:

$$\Delta G = \Delta H - T\Delta S$$

- Standard free-energy change:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG° for a reaction.

Answers

Exercise 19.5.1

At 25°C, the standard enthalpy change (ΔH°) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are

- S°(N_2H_4) = 121.2 J/(mol•K),
- S°(N_2) = 191.6 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Exercise 19.5.1

149.5 kJ/mol

no, not spontaneous

Video Solution

Exercise 19.5.2

92.8 kJ; no

Video Solution

Exercise 19.5.3

–72.5 kJ/mol of O_2

33.8 kJ/mol of O_2

Exercise 19.5.4

792.6 K

Video Solution

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19.6: Free Energy and Temperature

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for **both a system and its surroundings**. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Energy and Spontaneity

The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{19.6.1}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 19.6.1 to $\Delta G = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{19.6.2}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \\ &= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0\end{aligned}$$

Multiplying both sides of the inequality by –T reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0$$

which is equal to ΔG (Equation 19.6.1). We can therefore see that for a spontaneous process, $\Delta G < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 19.6.1 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657 J$, so the process is highly endothermic. From the definition of ΔS (Equation 19.6.2), we know that for 1 mol of water,

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} = \frac{40{,}657 \text{ J}}{373.15 \text{ K}} = 108.96 \text{ J/K}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\Delta G_{100^\circ\text{C}} = \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} = 40{,}657 \text{ J} - [(373.15 \text{ K})(108.96 \text{ J/K})] = 0 \text{ J}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\Delta G_{110^\circ\text{C}} = \Delta H - T\Delta S = 40{,}657 \text{ J} - [(383.15 \text{ K})(108.96 \text{ J/K})] = -1091 \text{ J}$$

At 110°C, ΔG < 0, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\Delta G_{90^\circ\text{C}} = \Delta H - T\Delta S = 40{,}657 \text{ J} - [(363.15 \text{ K})(108.96 \text{ J/K})] = 1088 \text{ J}$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ\text{C}} = 1090 \text{ J} = -\Delta G_{90^\circ\text{C}}$, as we would predict.

Equilibrium Conditions

ΔG = 0 only if ΔH = TΔS.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 19.6.1), setting ΔG = 0, and solving for T,

$$0 \text{ J} = 40{,}657 \text{ J} - T(108.96 \text{ J/K})$$
$$T = 373.15 \text{ K}$$

Thus ΔG = 0 at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 19.6.1 shows

how the ΔH and TΔS terms vary with temperature for the vaporization of water. When the two lines cross, ΔG = 0, and ΔH = TΔS.

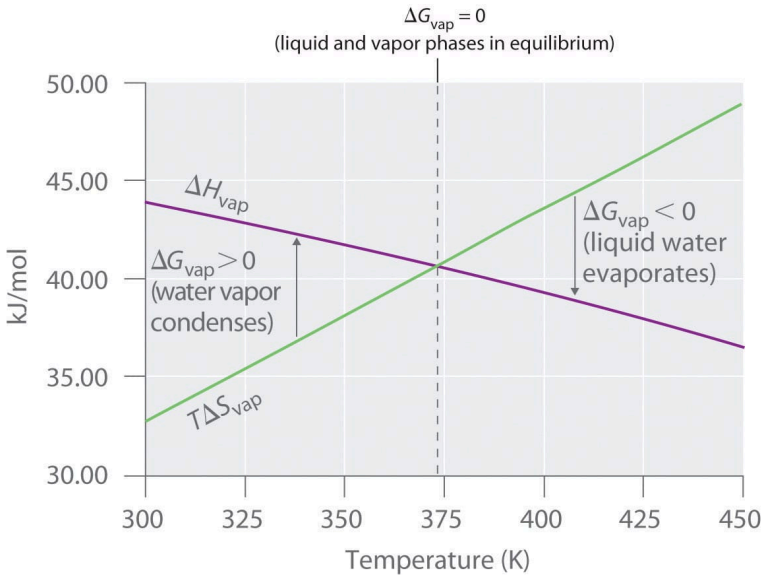


Figure 19.6.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH – TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

Graph of kilojoule per mole against temperature. The purple line is the delta H vaporization. the green line is the T delta S vaporization.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy (ΔH > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid (ΔS > 0). At temperatures greater than 373 K, the TΔS term dominates, and ΔG < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

Figure 19.6.1*:*

ΔH	ΔS	$-T\Delta S$	ΔG
- (exothermic)	+ (products more disordered)	- (favors spontaneity)	- (spontaneous at all T)
- (exothermic)	- (products less disordered)	+ (opposes spontaneity)	- (spontaneous) at low T + (non-spontaneous) at high T "Enthalpically-driven process"
+ (endothermic)	+ (products more disordered)	- (favors spontaneity)	+ (non-spontaneous) at low T - (spontaneous) at high T "Entropically-driven process"
+ (endothermic)	- (products less disordered)	+ (opposes spontaneity)	+ (non-spontaneous at all T)

YouTube Video

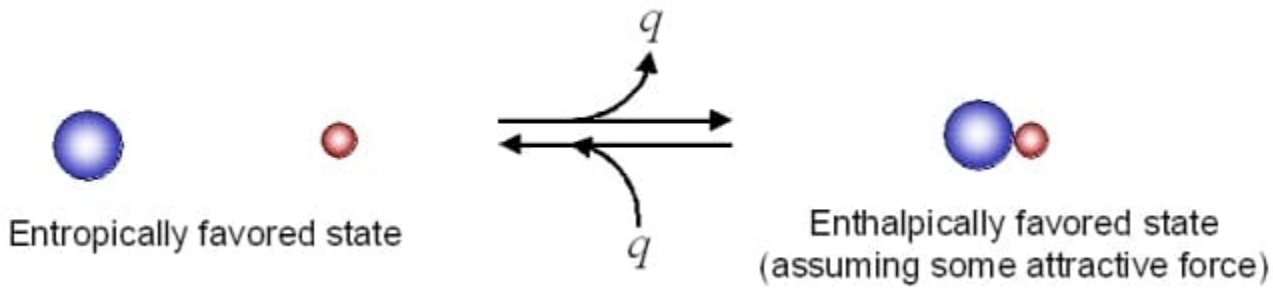
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Determining if a Reaction is Spontaneous: Determining if a Reaction is Spontaneous(opens in new window) [youtu.be]

Enthalpically vs. Entropically Driving Reactions

Consider the following possible states for two different types of molecules with some attractive force:

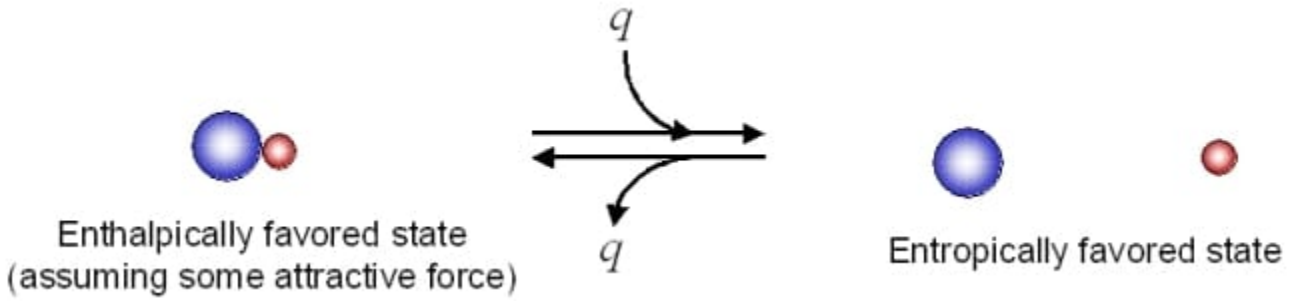


On the left is the entropically favored state where the two atoms are far away. On the right is the enthalpically favored state assuming some attractive force where the two atoms are attracted to each other.

There would appear to be greater entropy on the left (state 1) than on the right (state 2). Thus the entropic change for the reaction as written (i.e. going to the right) would be (-) in magnitude, and the energetic contribution to the free energy change would be (+) (i.e. unfavorable) for the reaction as written.

In going to the right, there is an attractive force and the molecules adjacent to each other is a lower energy state (heat energy, q, is liberated). To go to the left, we have to overcome this attractive force (input heat energy) and the left direction is unfavorable with regard to heat energy q. The change in enthalpy is (-) in going to the right (q released), and this enthalpy change is negative (-) in going to the right (and (+) in going to the left). This reaction as written, is therefore, **enthalpically favorable and entropically unfavorable**. Hence, it is an enthalpically driven reaction.

From Table 19.6.1, it would appear that we might be able to get the reaction to go to the right at low temperatures (lower temperature would minimize the energetic contribution of the entropic change). Looking at the same process from an opposite direction:



This reaction as written, is entropically favorable, and enthalpically unfavorable. It is an entropically driven reaction. From Table

19.6.1, it would appear that we might be able to get the reaction to go to the right at high temperatures (high temperature would increase the energetic contribution of the entropic change).

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 19.6.1. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{19.6.3}$$

This equation tells us that when energy is released during an exothermic process (ΔH < 0), such as during the combustion of a fuel, some of that energy can be used to do work (ΔG < 0), while some is used to increase the entropy of the universe (TΔS > 0). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 19.6.2, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 19.6.2: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard

enthalpy and entropy changes are known, using Equation 19.6.4:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{19.6.4}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG° means that the equilibrium constant is less than 1.

Example 19.6.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$\mathrm{H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O_2\,(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is –187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 19.6.4, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG° for the reaction, we need to know ΔH°, ΔS°, and T. We are given ΔH°, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the “products minus reactants” rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\text{ mol }\mathrm{H_2O_2} \times 109.6\text{ J/(mol}\cdot\mathrm{K})] \\ &\quad - \{[1\text{ mol }\mathrm{H_2} \times 130.7\text{ J/(mol}\cdot\mathrm{K})] + [1\text{ mol }\mathrm{O_2} \times 205.2\text{ J/(mol}\cdot\mathrm{K})]\} \\ &= -226.3\text{ J/K (per mole of }\mathrm{H_2O_2})\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS° is very negative for this reaction.

B Substituting the appropriate quantities into Equation 19.6.4,

$$\begin{aligned}\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ &= -187.78\text{ kJ/mol} - (298.15\text{ K})[-226.3\text{ J/(mol}\cdot\mathrm{K}) \times 1\text{ kJ/1000 J}] \\ &= -187.78\text{ kJ/mol} + 67.47\text{ kJ/mol} = -120.31\text{ kJ/mol}\end{aligned}$$

The negative value of ΔG° indicates that the reaction is spontaneous as written. Because ΔS° and ΔH° for this reaction have the same sign, the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS° term and for the energy needed to break bonds in the reactants.

Exercise 19.6.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l)$$

At 25°C, the standard enthalpy change (ΔH°) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are S°(N_2H_4) = 121.2 J/(mol•K), S°(N_2) = 191.6 J/(mol•K), and S°(H_2) = 130.7 J/(mol•K). Is the reaction spontaneous as written?

Answer available at the end of this section.

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG_f°)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G_f^\circ = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta_f^o = \Delta H_f^o - T\Delta S_f^o \tag{19.6.5}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

$$\Delta G_{rxn}^o = \sum m\Delta G_f^o(products) - \sum n\Delta_f^o(reactants) \tag{19.6.6}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

The "Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG°_f values (Table T1) using the “products minus reactants” rule.

Example 19.6.2

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water. Use the following data:

- ΔG°_f(isooctane) = –353.2 kJ/mol,
- $\Delta G^\circ_f(CO_2)$ = –394.4 kJ/mol, and
- $\Delta G^\circ_f(H_2O)$ = –237.1 kJ/mol. Is the reaction spontaneous as written?

Given: balanced chemical equation and values of ΔG°_f for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the “products minus reactants” rule to obtain ΔG°_{rxn}, remembering that $\Delta G°_f$ for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$$

We are given ΔG°_f values for all the products and reactants except $O_2(g)$. Because oxygen gas is an element in its standard state, $\Delta G^\circ_f (O_2)$ is zero. Using the “products minus reactants” rule,

$$\begin{aligned}\Delta G^\circ &= [8\Delta G^\circ_f(CO_2) + 9\Delta G^\circ_f(H_2O)] - \left[1\Delta G^\circ_f(C_8H_{18}) + \frac{25}{2}\Delta G^\circ_f(O_2)\right] \\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\ &- \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\ &= -4935.9\text{ kJ (per mol of } C_8H_{18})\end{aligned}$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Exercise 19.6.2

Calculate ΔG° for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer available at the end of this section.

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 19.6.3

Calculate (a) ΔG° and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)⟐2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),

- $S°(H_2)$ = 130.7 J/(mol•K),
- $S°(NH_3)$ = 192.8 J/(mol•K), and
- $\Delta H^\circ_f\ (NH_3)$ = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG° and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 19.6.4 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 19.6.1 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 19.6.4, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)] \\ &= [2\text{ mol NH}_3 \times 192.8\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol N}_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol H}_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\} \\ &= -198.1\text{ J/K (per mole of N}_2)\end{aligned}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of $\Delta H^\circ_f\ (NH_3)$ is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_f(\text{NH}_3) - [\Delta H^\circ_f(\text{N}_2) + 3\Delta H^\circ_f(\text{H}_2)] \\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})] \\ &= -91.8\text{ kJ(per mole of N}_2)\end{aligned}$$

B Inserting the appropriate values into Equation 19.6.4

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ - T\Delta S^\circ = (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) = -32.7\text{ kJ (per mole of N}_2)$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 19.6.1:

$$\begin{aligned}\Delta G_{300^\circ\text{C}} &= \Delta H_{300^\circ\text{C}} - (573\text{ K})(\Delta S_{300^\circ\text{C}}) = \Delta H^\circ - (573\text{ K})\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) = 21.7\text{ kJ (per mole of N}_2)\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the −TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

Exercise 19.6.3

Calculate

a. ΔG° and

b. $\Delta G_{750°C}$

for the following reaction

$$2NO(g) + O_2(g) <=> 2NO_2(g)$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- ΔH°_f(NO_2) = 33.2 kJ/mol, and
- ΔH°_f (NO) = 91.3 kJ/mol.

Answer a available at the end of this section.

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting ΔG° = 0 in Equation 19.6.4, as illustrated in Example 19.6.4.

Example 19.6.4

As you saw in Example 19.6.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 9.5.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG° equal to zero in Equation 19.6.4 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 19.6.3, we calculated that ΔH° is –91.8 kJ/mol of N_2 and ΔS° is –198.1 J/K per mole of N_2, corresponding to ΔG° = –32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG° equal to zero and rearranging Equation 19.6.4 to solve for T:

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 0 \\ \Delta H^\circ &= T\Delta S^\circ \\ T = \frac{\Delta H^\circ}{\Delta S^\circ} &= \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{-198.1\text{ J/K}} = 463\text{ K} \end{aligned}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise 19.6.4

As you found in the exercise in Example 9.5.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer available at the end of this section.

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change

$$\Delta G = \Delta H - T\Delta S$$

- Standard free-energy change

$$\Delta G° = \Delta H° - T\Delta S°$$

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG° for a reaction.

Contributors and Attributions

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- Mike Blaber (Florida State University)

Answers

Exercise 19.6.1
149.5 kJ/mol; no
Video Solution

Exercise 19.6.2
92.8 kJ; no
Video Solution

Exercise 19.6.3
–72.5 kJ/mol of O_2
33.8 kJ/mol of O_2
Video Solution

Exercise 19.6.4
792.6 K

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19.7: Free Energy and the Equilibrium Constant

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

1. $\Delta S_{univ} > 0$,
2. $\Delta G_{sys} < 0$ (applicable under constant temperature and constant pressure conditions), and
3. the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table $19.7.1$ summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table $19.7.1$: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
$Q < K$	$Q = K$	$Q > K$
***Spontaneous in the reverse direction.**		

Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG^o) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH^o and ΔS^o determine the magnitude and sign of ΔG^o and also because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG^o and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follows (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{19.7.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation $19.7.1$ simplifies to

$$\Delta G = V\Delta P \tag{19.7.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation $19.7.2$ by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{19.7.3}$$

$$= nRT\frac{\Delta P}{P} \tag{19.7.4}$$

$$= nRT\ln\left(\frac{P_\mathrm{f}}{P_\mathrm{i}}\right) \tag{19.7.5}$$

If the initial state is the standard state with $P_i = 1\ atm$, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^\circ = nRT\ln P$$

This can be rearranged as follows:

$$G = G^\circ + nRT\ln P \tag{19.7.6}$$

As you will soon discover, Equation 19.7.6 allows us to relate ΔG^o and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{19.7.7}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{19.7.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{19.7.9}$$

Substituting Equation 19.7.6 for each term into Equation 19.7.9,

$$\Delta G = [(cG^o_C + cRT\ln P_C) + (dG^o_D + dRT\ln P_D)] - [(aG^o_A + aRT\ln P_A) + (bG^o_B + bRT\ln P_B)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{P_\mathrm{C}^c P_\mathrm{D}^d}{P_\mathrm{A}^a P_\mathrm{B}^b}\right) \tag{19.7.10}$$

$$= \Delta G^\circ + RT\ln Q \tag{19.7.11}$$

where ΔG^o indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^o and K_p for gases as follows:

$$0 = \Delta G^o + RT\ln K_p \tag{19.7.12}$$

$$\Delta G^o = -RT\ln K_p \tag{19.7.13}$$

If the products and reactants are in their standard states and $\Delta G^o < 0$, then $K_p > 1$, and products are favored over reactants when the reaction is at equilibrium. Conversely, if $\Delta G^o > 0$, then $K_p < 1$, and reactants are favored over products when the reaction is at equilibrium. If $\Delta G^o = 0$, then $K_p = 1$, and neither reactants nor products are favored when the reaction is at equilibrium.

For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.

Example 19.7.1

ΔG^o is –32.7 kJ/mol of N_2 for the reaction

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm, and
- $T = 100^oC$.

Does the reaction proceed to the right, as written, or to the left to reach equilibrium?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether the reaction proceeds to the right or to the left to reach equilibrium

Strategy:

A. Using the values given and Equation 19.7.11, calculate Q.
B. Determine if Q is >, <, or = to K
C. Substitute the values of ΔG^o and Q into Equation 19.7.11 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG^o and ΔG under nonstandard conditions is given in Equation 19.7.11. Substituting the partial pressures given, we can calculate Q:

$$\begin{aligned} Q &= \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} \\ &= \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7} \end{aligned}$$

B Because ΔG^o is –, K must be a number greater than 1

C Substituting the values of ΔG^o and Q into Equation 19.7.11,

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= -32.7\ \text{kJ} + \left[(8.314\ \text{J/K})(373\ \text{K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)\ln(6.4 \times 10^{-7})\right] \\ &= -32.7\ \text{kJ} + (-44\ \text{kJ}) \\ &= -77\ \text{kJ/mol of } N_2 \end{aligned}$$

Because $\Delta G < 0$ and $Q < K$ (because $Q < 1$), the reaction proceeds spontaneously to the right, as written, in order to reach equilibrium.

Exercise 19.7.1

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and $P_{NO_2} = 1.00 \times 10^{-4} atm$. The value of ΔG^o for this reaction is –72.5 kJ/mol of O_2. Are products or reactants favored?

Answer available at the end of this section.

Example 19.7.2

Calculate K_p for the reaction of $\mathrm{H_2}$ with $\mathrm{N_2}$ to give $\mathrm{NH_3}$ at 25°C. ΔG^o for this reaction is –32.7 kJ/mol of $\mathrm{N_2}$.

Given: balanced chemical equation from Example 19.7.1, ΔG^o, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG^o and T (in kelvin) into Equation 19.7.13 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 19.7.1, we used tabulated values of ΔG°_f to calculate ΔG^o for this reaction (–32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 19.7.13,

$$\Delta G^\circ = -RT \ln K_\mathrm{p}$$
$$\frac{-\Delta G^\circ}{RT} = \ln K_\mathrm{p}$$

Inserting the value of ΔG^o and the temperature (25°C = 298 K) into this equation,

$$\ln K_\mathrm{p} = -\frac{(-32.7\ \mathrm{kJ})(1000\ \mathrm{J/kJ})}{(8.314\ \mathrm{J/K})(298\ \mathrm{K})} = 13.2$$
$$K_\mathrm{p} = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is product-favored. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

Exercise 19.7.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG^o for this reaction is –70.5 kJ/mol of $\mathrm{O_2}$.

Answer available at the end of this section.

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. The numerical magnitude of K_p and K are related:

$$K_p = K(RT)^{\Delta n} \tag{19.7.14}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 19.7.13 can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \tag{19.7.15}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 19.7.15 for the difference between K_p and K.

Non-Ideal Behavior

Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equation 19.7.15 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG^o influence the magnitude of the equilibrium constant:

$$\Delta G° = \Delta H° - T\Delta S° \tag{19.7.16}$$

$$= -RT \ln K \tag{19.7.17}$$

Notice that K becomes larger as ΔS^o becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH^o decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum entropy and seek the lowest energy state possible.

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Relating Grxn and Kp: Relating Grxn and Kp(opens in new window) [youtu.be]

Temperature Dependence of the Equilibrium Constant

The fact that ΔG^o and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 19.7.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{19.7.18}$$

Assuming ΔH^o and ΔS^o are temperature independent, for an exothermic reaction ($\Delta H^o < 0$), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 19.7.18 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 19.7.18 also shows that the magnitude of ΔH^o dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS^o affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH^o for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS^o. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 19.7.18 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H°}{RT_1} + \frac{\Delta S°}{R}$$

and

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{19.7.19}$$

Thus calculating ΔH^o from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH^o and ΔS^o are independent of temperature.

Example 19.7.4

The equilibrium constant for the formation of $\mathrm{NH_3}$ from $\mathrm{H_2}$ and $\mathrm{N_2}$ at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 19.7.3. What is K_p at 500°C? (Use the data from Example 19.7.1.)

Given: balanced chemical equation, ΔH^o °, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 19.7.19 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH^o for the reaction obtained using Hess's law is –91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298.K and T_2 = 500°C = 773 K, then from Equation 19.7.19 we obtain the following:

$$\begin{aligned}
\ln \frac{K_2}{K_1} &= \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \\
&= \frac{(-91.8\ \mathrm{kJ})(1000\ \mathrm{J/kJ})}{8.314\ \mathrm{J/K}}\left(\frac{1}{298\ \mathrm{K}} - \frac{1}{773\ \mathrm{K}}\right) = -22.8 \\
\frac{K_2}{K_1} &= 1.3 \times 10^{-10} \\
K_2 &= (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}
\end{aligned}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise 19.7.4

In the exercise in Example 19.7.3, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the ΔH_f^o values in the exercise in Example 19.7.1 to calculate K_p for this reaction at 1000°C.

Answer available at the end of this section.

YouTube Video

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The Van't Hoff Equation: The Van't Hoff Equation (opens in new window) [youtu.be]

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If $\Delta G^o < 0$, then K > 1, and products are favored over reactants at equilibrium. Conversely, if $\Delta G^o > 0$, then K < 1, and reactants are favored over products at equilibrium. If $\Delta G^o = 0$, then K=1, and neither reactants nor products are favored at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors and Attributions

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- Modified by Tom Neils (Grand Rapids Community College)

Answers

Exercise 19.7.1

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written. The reaction will proceed in the forward direction to reach equilibrium.

Exercise 19.7.3

2.3×10^{12}

Exercise 19.7.4

5.6×10^{-4}

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19.E: Chemical Thermodynamics (Exercises)

19.1: Spontaneous Processes

19.2: Entropy and the Second Law of Thermodynamics

Conceptual Problems

1. A Russian space vehicle developed a leak, which resulted in an internal pressure drop from 1 atm to 0.85 atm. Is this an example of a reversible expansion? Has work been done?
2. Which member of each pair do you expect to have a higher entropy? Why?

    a. solid phenol or liquid phenol
    b. 1-butanol or butane
    c. cyclohexane or cyclohexanol
    d. 1 mol of N_2 mixed with 2 mol of O_2 or 2 mol of NO_2
    e. 1 mol of O_2 or 1 mol of O_3
    f. 1 mol of propane at 1 atm or 1 mol of propane at 2 atm

3. Determine whether each process is reversible or irreversible.

    a. ice melting at 0°C
    b. salt crystallizing from a saline solution
    c. evaporation of a liquid in equilibrium with its vapor in a sealed flask
    d. a neutralization reaction

4. Determine whether each process is reversible or irreversible.

    a. cooking spaghetti
    b. the reaction between sodium metal and water
    c. oxygen uptake by hemoglobin
    d. evaporation of water at its boiling point

5. Explain why increasing the temperature of a gas increases its entropy. What effect does this have on the internal energy of the gas?

6. For a series of related compounds, does ΔS_{vap} increase or decrease with an increase in the strength of intermolecular interactions in the liquid state? Why?

7. Is the change in the enthalpy of reaction or the change in entropy of reaction more sensitive to changes in temperature? Explain your reasoning.

8. Solid potassium chloride has a highly ordered lattice structure. Do you expect ΔS_{soln} to be greater or less than zero? Why? What opposing factors must be considered in making your prediction?

9. Aniline ($C_6H_5NH_2$) is an oily liquid at 25°C that darkens on exposure to air and light. It is used in dying fabrics and in staining wood black. One gram of aniline dissolves in 28.6 mL of water, but aniline is completely miscible with ethanol. Do you expect ΔS_{soln} in H_2O to be greater than, less than, or equal to ΔS_{soln} in CH_3CH_2OH? Why?

Conceptual Answers

1. No, it is irreversible; no work is done because the external pressure is effectively zero.
3.

a. reversible
b. irreversible
c. reversible
d. irreversible

9. Water has a highly ordered, hydrogen-bonded structure that must reorganize to accommodate hydrophobic solutes like aniline. In contrast, we expect that aniline will be able to disperse randomly throughout ethanol, which has a significantly less ordered structure. We therefore predict that ΔS_{soln} in ethanol will be more positive than ΔS_{soln} in water.

Numerical Problems

1. Liquid nitrogen, which has a boiling point of –195.79°C, is used as a coolant and as a preservative for biological tissues. Is the entropy of nitrogen higher or lower at –200°C than at –190°C? Explain your answer. Liquid nitrogen freezes to a white solid at –210.00°C, with an enthalpy of fusion of 0.71 kJ/mol. What is its entropy of fusion? Is freezing biological tissue in liquid nitrogen an example of a reversible process or an irreversible process?
2. Using the second law of thermodynamics, explain why heat flows from a hot body to a cold body but not from a cold body to a hot body.
3. One test of the spontaneity of a reaction is whether the entropy of the universe increases: $\Delta S_{univ} > 0$. Using an entropic argument, show that the following reaction is spontaneous at 25°C:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Why does the entropy of the universe increase in this reaction even though gaseous molecules, which have a high entropy, are consumed?

4. Calculate the missing data in the following table.

Compound	ΔH_{fus} (kJ/mol)	ΔS_{fus} [J/(mol·K)]	Melting Point (°C)
acetic acid	11.7		16.6
CH_3CN	8.2	35.9	
CH_4	0.94		–182.5
CH_3OH		18.2	–97.7
formic acid	12.7	45.1	

Based on this table, can you conclude that entropy is related to the nature of functional groups? Explain your reasoning.

5. Calculate the missing data in the following table.

Compound	ΔH_{vap} (kJ/mol)	ΔS_{vap} [J/(mol·K)]	Boiling Point (°C)
hexanoic acid	71.1		105.7
hexane	28.9	85.5	
formic acid		60.7	100.8
1-hexanol	44.5		157.5

The text states that the magnitude of ΔS_{vap} tends to be similar for a wide variety of compounds. Based on the values in the table, do you agree?

19.3: The Molecular Interpretation of Entropy

19.4: Entropy Changes in Chemical Reactions

19.5: Gibbs Free Energy

Conceptual Problems

1. How does each example illustrate the fact that no process is 100% efficient?

    a. burning a log to stay warm
    b. the respiration of glucose to provide energy
    c. burning a candle to provide light

2. Neither the change in enthalpy nor the change in entropy is, by itself, sufficient to determine whether a reaction will occur spontaneously. Why?

3. If a system is at equilibrium, what must be the relationship between ΔH and ΔS?

4. The equilibrium $2AB \diamondsuit A_2B_2$ is exothermic in the forward direction. Which has the higher entropy—the products or the reactants? Why? Which is favored at high temperatures?

5. Is ΔG a state function that describes a system or its surroundings? Do its components—ΔH and ΔS—describe a system or its surroundings?

6. How can you use ΔG to determine the temperature of a phase transition, such as the boiling point of a liquid or the melting point of a solid?

7. Occasionally, an inventor claims to have invented a “perpetual motion” machine, which requires no additional input of energy once the machine has been put into motion. Using your knowledge of thermodynamics, how would you respond to such a claim? Justify your arguments.

8. Must the entropy of the universe increase in a spontaneous process? If not, why is no process 100% efficient?

9. The reaction of methyl chloride with water produces methanol and hydrogen chloride gas at room temperature, despite the fact that $\Delta H^\circ_{rxn} = 7.3$ kcal/mol. Using thermodynamic arguments, propose an explanation as to why methanol forms.

Conceptual Answers

9. In order for the reaction to occur spontaneously, ΔG for the reaction must be less than zero. In this case, ΔS must be positive, and the $T\Delta S$ term outweighs the positive value of ΔH.

Numerical Problems

1. Use the tables in the text to determine whether each reaction is spontaneous under standard conditions. If a reaction is not spontaneous, write the corresponding spontaneous reaction.

    a. $\mathrm{H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)}$
    b. $2H_2(g) + C_2H_2(g) \rightarrow C_2H_6(g)$
    c. $(CH_3)_2O(g) + H_2O(g) \rightarrow 2CH_3OH(l)$
    d. $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

2. Use the tables in the text to determine whether each reaction is spontaneous under standard conditions. If a reaction is not spontaneous, write the corresponding spontaneous reaction.

a. $K_2O_2(s) \rightarrow 2K(s) + O_2(g)$
b. $PbCO_3(s) \rightarrow PbO(s) + CO_2(g)$
c. $P_4(s) + 6H_2(g) \rightarrow 4PH_3(g)$
d. $2AgCl(s) + H_2S(g) \rightarrow Ag_2S(s) + 2HCl(g)$

3. Nitrogen fixation is the process by which nitrogen in the atmosphere is reduced to NH_3 for use by organisms. Several reactions are associated with this process; three are listed in the following table. Which of these are spontaneous at 25°C? If a reaction is not spontaneous, at what temperature does it become spontaneous?

Reaction	ΔH°_{298} (kcal/mol)	ΔS°_{298} [cal/(°·mol)]
(a) $\frac{1}{2}N_2 + O_2 \rightarrow NO_2$	8.0	−14.4
(b) $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO$	21.6	2.9
(c) $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$	−11.0	−23.7

4. A student was asked to propose three reactions for the oxidation of carbon or a carbon compound to CO or CO_2. The reactions are listed in the following table. Are any of these reactions spontaneous at 25°C? If a reaction does not occur spontaneously at 25°C, at what temperature does it become spontaneous?

Reaction	ΔH°_{298} (kcal/mol)	ΔS°_{298} [cal/(°·mol)]
$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$	42	32
$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$	−9.8	−10.1
$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$	49.3	51.3

5. Tungsten trioxide (WO_3) is a dense yellow powder that, because of its bright color, is used as a pigment in oil paints and water colors (although cadmium yellow is more commonly used in artists' paints). Tungsten metal can be isolated by the reaction of WO_3 with H_2 at 1100°C according to the equation $WO_3(s) + 3H_2(g) \rightarrow W(s) + 3H_2O(g)$. What is the lowest temperature at which the reaction occurs spontaneously? $\Delta H° = 27.4$ kJ/mol and $\Delta S° = 29.8$ J/K.

6. Sulfur trioxide (SO_3) is produced in large quantities in the industrial synthesis of sulfuric acid. Sulfur dioxide is converted to sulfur trioxide by reaction with oxygen gas.

a. Write a balanced chemical equation for the reaction of SO_2 with $O_2(g)$ and determine its $\Delta G°$.
b. What is the value of the equilibrium constant at 600°C?
c. If you had to rely on the equilibrium concentrations alone, would you obtain a higher yield of product at 400°C or at 600°C?

7. Calculate $\Delta G°$ for the general reaction $MCO_3(s) \rightarrow MO(s) + CO_2(g)$ at 25°C, where M is Mg or Ba. At what temperature does each of these reactions become spontaneous?

Compound	ΔH°_f (kJ/mol)	S° [J/(mol·K)]
MCO_3		
Mg	−1111	65.85
Ba	−1213.0	112.1
MO		
Mg	−601.6	27.0
Ba	−548.0	72.1
CO_2	−393.5	213.8

8. The reaction of aqueous solutions of barium nitrate with sodium iodide is described by the following equation:

$$Ba(NO_3)_2(aq) + 2NaI(aq) \rightarrow BaI_2(aq) + 2NaNO_3(aq)$$

You want to determine the absolute entropy of BaI_2, but that information is not listed in your tables. However, you have been able to obtain the following information:

	$Ba(NO_3)_2$	NaI	BaI_2	$NaNO_3$
ΔH°_f (kJ/mol)	−952.36	−295.31	−605.4	−447.5
S° [J/(mol·K)]	302.5	170.3		205.4

You know that ΔG° for the reaction at 25°C is 22.64 kJ/mol. What is ΔH° for this reaction? What is S° for BaI_2?

Numerical Answers

1.

a. −237.1 kJ/mol; spontaneous as written
b. −241.9 kJ/mol; spontaneous as written
c. 8.0 kJ/mol; spontaneous in reverse direction.
d. 141.9 kJ/mol; spontaneous in reverse direction.

3.

a. Not spontaneous at any T
b. Not spontaneous at 25°C; spontaneous above 7400 K
c. Spontaneous at 25°C

5. 919 K

7. $MgCO_3$: ΔG° = 63 kJ/mol, spontaneous above 663 K; $BaCO_3$: ΔG° = 220 kJ/mol, spontaneous above 1562 K

19.6: Free Energy and Temperature

19.7: Free Energy and the Equilibrium Constant

Conceptual Problems

1. Do you expect products or reactants to dominate at equilibrium in a reaction for which ΔG° is equal to

a. 1.4 kJ/mol?
b. 105 kJ/mol?
c. −34 kJ/mol?

2. The change in free energy enables us to determine whether a reaction will proceed spontaneously. How is this related to the extent to which a reaction proceeds?

3. What happens to the change in free energy of the reaction $N_2(g) + 3F_2(g) \rightarrow 2NF_3(g)$ if the pressure is increased while the temperature remains constant? if the temperature is increased at constant pressure? Why are these effects not so important for reactions that involve liquids and solids?

4. Compare the expressions for the relationship between the change in free energy of a reaction and its equilibrium constant where the reactants are gases versus liquids. What are the differences between these expressions?

Numerical Problems

1. Carbon monoxide, a toxic product from the incomplete combustion of fossil fuels, reacts with water to form CO_2 and H_2, as shown in the equation $CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$, for which $\Delta H° = -41.0$ kJ/mol and $\Delta S° = -42.3$ J cal/(mol·K) at 25°C and 1 atm.

    a. What is $\Delta G°$ for this reaction?
    b. What is ΔG if the gases have the following partial pressures: $P_{CO} = 1.3$ atm, $P_{H_2O} = 0.8$ atm, $P_{CO_2} = 2.0$ atm, and $P_{H_2} = 1.3$ atm?
    c. What is ΔG if the temperature is increased to 150°C assuming no change in pressure?

2. Methane and water react to form carbon monoxide and hydrogen according to the equation $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$.

    a. What is the standard free energy change for this reaction?
    b. What is K_p for this reaction?
    c. What is the carbon monoxide pressure if 1.3 atm of methane reacts with 0.8 atm of water, producing 1.8 atm of hydrogen gas?
    d. What is the hydrogen gas pressure if 2.0 atm of methane is allowed to react with 1.1 atm of water?
    e. At what temperature does the reaction become spontaneous?

3. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.

    a. $CCl_4(g)+6H_2O(l) \rightleftharpoons CO_2(g)+4HCl(aq)$; $\Delta G° = -377$ kJ/mol
    b. $Xe(g)+2F_2(g) \rightleftharpoons XeF_4(s)$; $\Delta H° = -66.3$ kJ/mol, $\Delta S° = -102.3$ J/(mol·K)
    c. $PCl_3(g)+S \rightleftharpoons PSCl_3(l)$; $\Delta G°_f(PCl_3) = -272.4$ kJ/mol, $\Delta G°_f (PSCl_3) = -363.2$ kJ/mol

4. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.

    a. $2KClO_3(s) \rightleftharpoons 2KCl(s)+3O_2(g)$; $\Delta G° = -225.8$ kJ/mol
    b. $CoCl_2(s)+6H_2O(g) \rightleftharpoons CoCl_2 \cdot 6H_2O(s)$; $\Delta H°_{rxn} = -352$ kJ/mol, $\Delta S°_{rxn} = -899$ J/(mol·K)
    c. $2PCl_3(g)+O_2(g) \rightleftharpoons 2POCl_3(g)$; $\Delta G°_f(PCl_3) = -272.4$ kJ/mol, $\Delta G°_f (POCl_3) = -558.5$ kJ/mol

5. The gas-phase decomposition of N_2O_4 to NO_2 is an equilibrium reaction with $K_p = 4.66 \times 10^{-3}$. Calculate the standard free-energy change for the equilibrium reaction between N_2O_4 and NO_2.

6. The standard free-energy change for the dissolution $K_4Fe(CN)_6 \cdot H_2O(s) \rightleftharpoons 4K^+(aq)+Fe(CN)_6{}^{4-}(aq)+H_2O(l)$ is 26.1 kJ/mol. What is the equilibrium constant for this process at 25°C?

7. Ammonia reacts with water in liquid ammonia solution (am) according to the equation $NH_3(g) + H_2O(am) \rightleftharpoons NH_4{}^+(am) + OH^-(am)$. The change in enthalpy for this reaction is 21 kJ/mol, and $\Delta S° = -303$ J/(mol·K). What is the equilibrium constant for the reaction at the boiling point of liquid ammonia (−31°C)?

8. At 25°C, a saturated solution of barium carbonate is found to have a concentration of $[Ba^{2+}] = [CO_3{}^{2-}] = 5.08 \times 10^{-5}$ M. Determine $\Delta G°$ for the dissolution of $BaCO_3$.

9. Lead phosphates are believed to play a major role in controlling the overall solubility of lead in acidic soils. One of the dissolution reactions is $Pb_3(PO_4)_2(s)+4H^+(aq) \rightleftharpoons 3Pb^{2+}(aq)+2H_2PO_4{}^-(aq)$, for which $\log K = -1.80$. What is $\Delta G°$ for this reaction?

10. The conversion of butane to 2-methylpropane is an equilibrium process with $\Delta H° = -2.05$ kcal/mol and $\Delta G° = -0.89$ kcal/mol.

    a. What is the change in entropy for this conversion?
    b. Based on structural arguments, are the sign and magnitude of the entropy change what you would expect? Why?

c. What is the equilibrium constant for this reaction?

11. The reaction of $CaCO_3(s)$ to produce $CaO(s)$ and $CO_2(g)$ has an equilibrium constant at 25°C of 2×10^{-23}. Values of ΔH°_f are as follows: $CaCO_3$, −1207.6 kJ/mol; CaO, −634.9 kJ/mol; and CO_2, −393.5 kJ/mol.

    a. What is ΔG° for this reaction?
    b. What is the equilibrium constant at 900°C?
    c. What is the partial pressure of $CO_2(g)$ in equilibrium with CaO and $CaCO_3$ at this temperature?
    d. Are reactants or products favored at the lower temperature? at the higher temperature?

12. In acidic soils, dissolved Al^{3+} undergoes a complex formation reaction with SO_4^{2-} to form $[AlSO_4^+]$. The equilibrium constant at 25°C for the reaction $Al^{3+}(aq)+SO_4^{2-}(aq) \diamondsuit AlSO_4^+(aq)$ is 1585.

    a. What is ΔG° for this reaction?
    b. How does this value compare with ΔG° for the reaction $Al^{3+}(aq)+F^-(aq) \diamondsuit AlF^{2+}(aq)$, for which $K = 10^7$ at 25°C?
    c. Which is the better ligand to use to trap Al^{3+} from the soil?

Numerical Answers

1.
    a. −28.4 kJ/mol
    b. −26.1 kJ/mol
    c. −19.9 kJ/mol
3.
    a. 1.21×10^{66}; equilibrium lies far to the right.
    b. 1.89×10^{6}; equilibrium lies to the right.
    c. 5.28×10^{16}; equilibrium lies far to the right.

5. 13.3 kJ/mol

7. 5.1×10^{-21}

9. 10.3 kJ/mol
11.
    a. 129.5 kJ/mol
    b. 6
    c. 6.0 atm
    d. Products are favored at high T; reactants are favored at low T.

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20: ELECTROCHEMISTRY

In oxidation–reduction (redox) reactions, electrons are transferred from one species (the reductant) to another (the oxidant). This transfer of electrons provides a means for converting chemical energy to electrical energy or vice versa. The study of the relationship between electricity and chemical reactions is called electrochemistry. In this chapter, we describe electrochemical reactions in more depth and explore some of their applications. We start by describing how they can be used to generate an electrical potential, or *voltage*; and discuss factors that affect the magnitude of the potential. We then explore the relationships among the electrical potential, the change in free energy, and the equilibrium constant for a redox reaction, which are all measures of the thermodynamic driving force for a reaction. Finally, we examine two kinds of applications of electrochemical principles: (1) those in which a spontaneous reaction is used to provide electricity and (2) those in which electrical energy is used to drive a thermodynamically nonspontaneous reaction.

By the end of this chapter, you will understand why different kinds of batteries are used in cars, flashlights, cameras, and portable computers; how rechargeable batteries operate; and why corrosion occurs and how to slow—if not prevent—it. You will also discover how metal objects can be plated with silver or chromium for protection; how silver polish removes tarnish; and how to calculate the amount of electricity needed to produce aluminum, chlorine, copper, and sodium on an industrial scale.

20.1: Oxidation States and Redox Reactions

20.2: Balanced Oxidation-Reduction Equations

20.3: Voltaic Cells

20.4: Cell Potential Under Standard Conditions

20.5: Gibbs Energy and Redox Reactions

20.6: Cell Potential Under Nonstandard Conditions

20.7: Batteries and Fuel Cells

20.8: Corrosion

20.9: Electrolysis

20.E: Electrochemistry (Exercises)

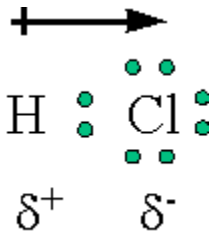
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20.1: Oxidation States and Redox Reactions

Electron transfer is one of the most basic processes that can happen in chemistry. It simply involves the movement of an electron from one atom to another. Many important biological processes rely on electron transfer, as do key industrial transformations used to make valuable products. In biology, for example, electron transfer plays a central role in respiration and the harvesting of energy from glucose, as well as the storage of energy during photosynthesis. In society, electron transfer has been used to obtain metals from ores since the dawn of civilization.

Oxidation States (Numbers)

Oxidation state is a useful tool for keeping track of electron transfers. It is most commonly used in dealing with metals and especially with transition metals. Unlike metals from the first two columns of the periodic table, such as sodium or magnesium, transition metals can often transfer different numbers of electrons, leading to different metal ions (e.g., sodium is generally found as $\mathrm{Na^+}$ and magnesium is almost always $\mathrm{Mg^{2+}}$, but manganese could be $\mathrm{Mn^{2+}}$, $\mathrm{Mn^{3+}}$, and so on, as far as $\mathrm{Mn^{7+}}$). Oxidation state is a number assigned to an element in a compound according to some rules. This number enables us to describe oxidation-reduction reactions, and balancing redox chemical reactions. When a covalent bond forms between two atoms with different electronegativities the shared electrons in the bond lie closer to the more electronegative atom:



For hydrochloric acid, the hydrogen is positive while the chlorine is negative. The dipole starts at the hydrogen and points towards the chlorine.

The **oxidation state** of an atom is the charge that results when the electrons in a covalent bond are assigned to the more electronegative atom and is the charge an atom would possess *if the bonding were ionic*. In HCl (above) the oxidation number for the hydrogen would be +1 and that of the Cl would be -1.

Example 20.1.1

Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the Oxidation State of each):

a. $\mathrm{Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2}$
b. $\mathrm{2\,Al + 3\,Cu^{2+} \longrightarrow 2\,Al^{3+} + 3\,Cu}$
c. $\mathrm{{CO_3}^{2-} + 2\,H^+ \longrightarrow CO_2 + H_2O}$

Solutions

a. Zn is oxidized (Oxidation number: 0 → +2); $\mathrm{H^+}$ is reduced (Oxidation number: +1 → 0)
b. Al is oxidized (Oxidation number: 0 → +3); $\mathrm{Cu^{2+}}$ is reduced (+2 → 0)
c. This is not a redox reaction because each element has the same oxidation number in both reactants and products: O= -2, H= +1, C= +4.

An atom is oxidized if its oxidation number increases, and an atom is reduced if its oxidation number decreases. The atom that is oxidized is the reducing agent, and the atom that is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound).

Oxidation Numbers and Nomenclature

Compounds of the alkali (oxidation number +1) and alkaline earth metals (oxidation number +2) are typically ionic in nature. Compounds of metals with higher oxidation numbers (e.g., tin +4) tend to form molecular compounds

- In ionic and covalent molecular compounds usually the ***less electronegative element is given first***.
- In ionic compounds the names are given which refer to ***the oxidation (ionic) state***
- In molecular compounds the names are given which refer ***to the number of molecules present in the compound***

Figure 20.1.1*: Example of nomenclature based on oxidation states.*

Ionic		Molecular	
MgH_2	magnesium hydride	H_2S	dihydrogen sulfide
FeF_2	iron(II) fluoride	OF_2	oxygen difluoride
Mn_2O_3	manganese(III) oxide	Cl_2O_3	dichlorine trioxide

An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

Oxidation-Reduction Reaction Examples

Redox reactions are comprised of two parts, a reduced half and an oxidized half, that *always* occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases. Simple ways to remember this include the mnemonic devices **OIL RIG,** meaning "*oxidation is loss*" and "*reduction is gain,*" and **LEO says GER,** meaning "*loss of* e^- = *oxidation*" and "*gain of* e^- = *reduced.*" There is no net change in the number of electrons in a redox reaction. Those given off in the oxidation half reaction are taken up by another species in the reduction half reaction.

The two species that exchange electrons in a redox reaction are given special names. The ion or molecule that accepts electrons is called the **oxidizing agent**; by accepting electrons it causes the oxidation of another species. Conversely, the species that donates electrons is called the **reducing agent**; when the reaction occurs, it reduces the other species. In other words, what is oxidized is the reducing agent and what is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound, as in disproportionation reactions).



Figure 20.1.1: A thermite reaction taking place on a cast iron skillet. A thermite reaction, using about 110 g of the mixture, taking place. The cast-iron skillet was destroyed in the process. (CC BY-SA 2.5 generic; Schuyler S via Wikipedia).

A good example of a redox reaction is the thermite reaction, in which iron atoms in ferric oxide lose (or give up) O atoms to Al atoms, producing $\mathrm{Al_2O_3}$ (Figure $20.1.1$).

$$\mathrm{Fe_2O_3\,(s) + 2\,Al\,(s) \longrightarrow Al_2O_3\,(s) + 2\,Fe\,(l)}$$

Another example of the redox reaction (although less dangerous) is the reaction between zinc and copper sulfate.

$$\mathrm{Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu}$$

Example $20.1.2$: Identifying Oxidized and Reduced Elements

Determine what is oxidized and what is reduced in the following reaction.

$$\mathrm{Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2}$$

Solution

The oxidation state of $\mathrm{H^+}$ changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2. Hence, Zn is oxidized and acts as the reducing agent.

The oxidation state of $\mathrm{H^+}$ changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2. Hence, $\mathrm{H^+}$ ion is reduced and acts as the oxidizing agent.

Combination Reactions

Combination reactions are among the simplest redox reactions and, as the name suggests, involves "combining" elements to form a chemical compound. As usual, oxidation and reduction occur together. The general equation for a combination reaction is given below:

$$\mathrm{A + B \rightarrow AB}$$

Example $20.1.3$: Combination Reaction

Equation:

$$\mathrm{H_2 + O_2 \longrightarrow H_2O}$$

Calculation: 0 + 0 → **(2)(+1) + (-2) = 0**

Explanation:

In this equation both $\mathrm{H_2}$ and $\mathrm{O_2}$ are free elements; following Rule #1, their Oxidation States are 0. The product is $\mathrm{H_2O}$, which has a total Oxidation State of 0. According to Rule #6, the Oxidation State of oxygen is usually -2. Therefore, the Oxidation State of H in $\mathrm{H_2O}$ must be +1.

Decomposition Reactions

A decomposition reaction is the reverse of a combination reaction, the breakdown of a chemical compound into individual elements:

$$AB \rightarrow A + B$$

Example $20.1.4$: Decomposition Reaction

Identify the oxidation state of the products and reactant in the decomposition of water:

$$H_2O \rightarrow H_2 + O_2$$

Calculation

$$(2)(+1) + (-2) = 0 \rightarrow 0 + 0$$

In this reaction, water is "decomposed" into hydrogen and oxygen. As in the previous example the H_2O has a total Oxidation State of 0; thus, according to Rule #6 the Oxidation State of oxygen is usually -2, so the Oxidation State of hydrogen in H_2O must be +1.

Single Replacement Reactions

A single replacement reaction involves the "replacing" of an element in the reactants with another element in the products:

\[\ce{A + BC \rightarrow AB + C} \nonumber \]

Example 20.1.5: Single Replacement Reaction

Chlorine gas is a great oxidizing agent and will replace bromide ions from sodium bromide salt.

$$\mathrm{Cl_2\,(g) + Na\ \underline{\mathit{Br}}\,(s) \longrightarrow Na\underline{\mathit{Cl}}\,(s) + Br_2\,(l)}$$

Explanation

In this equation, Br is replaced with Cl, and the Cl atoms in $\mathrm{Cl_2}$ are reduced, while the Br ion in NaBr is oxidized.

Double Replacement Reactions

A double replacement reaction is similar to a single replacement reaction, but involves "replacing" two elements in the reactants, with two in the products:

\[\ce{AB + CD \rightarrow AD + CB} \nonumber \]

Example 20.1.6: Double Replacement Reaction

The reaction of gaseous hydrogen chloride and iron oxide is a double replacement reaction. Write the expected reaction for this chemistry equation.

Solution

$$\mathrm{Fe_2O_3 + 6\,HCl \longrightarrow 2\,FeCl_3 + 3\,H_2O}$$

In this equation, Fe and H trade places, and oxygen and chlorine trade places.

Combustion Reactions

Combustion reactions almost always involve oxygen in the form of O_2, and are almost always exothermic, meaning they produce heat. Chemical reactions that give off light and heat and light are colloquially referred to as "burning."

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O$$

Although combustion reactions typically involve redox reactions with a chemical being oxidized by oxygen, many chemicals "burn" in other environments. For example, both titanium and magnesium burn in nitrogen as well:

$$2\,\mathrm{Ti\,(s)} + \mathrm{N_2\,(g)} \longrightarrow 2\,\mathrm{TiN\,(s)}$$

$$3\,\mathrm{Mg\,(s)} + \mathrm{N_2\,(g)} \longrightarrow \mathrm{Mg_3N_2\,(s)}$$

Moreover, chemicals can be oxidized by other chemicals than oxygen, such as $\mathrm{Cl_2}$ or $\mathrm{F_2}$; these processes are also considered combustion reactions

Disproportionation Reactions

A single substance can be both oxidized and reduced in some redox reactions. These are known as **disproportionation reactions**, with the following general equation:

$$2\,\mathrm{A} \longrightarrow \mathrm{A}^{+n} + \mathrm{A}^{-n}$$

where n is the number of electrons transferred. Disproportionation reactions do not need begin with neutral molecules, and can involve more than two species with differing oxidation states (but rarely).

Example 20.1.7: Disproportionation Reaction

Disproportionation reactions have some practical significance in everyday life, including the reaction of hydrogen peroxide, $\mathrm{H_2O_2}$ poured over a cut. This is a decomposition reaction of hydrogen peroxide (catalyzed by the catalase enzyme) that produces oxygen and water. Oxygen is present in all parts of the chemical equation and as a result it is both oxidized and reduced. The reaction is as follows:

$$2\,\mathrm{H_2O_2\,(aq)} \rightarrow 2\,\mathrm{H_2O\,(l)} + \mathrm{O_2\,(g)}$$

Explanation

On the reactant side, H has an Oxidation State of +1 and O has an Oxidation State of -1, which changes to -2 for the product $\mathrm{H_2O}$ (oxygen is reduced), and 0 in the product $\mathrm{O_2}$ (oxygen is oxidized).

YouTube Video

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Summary

Oxidation signifies a loss of electrons and reduction signifies a gain of electrons. Balancing redox reactions is an important step that changes in neutral, basic, and acidic solutions. The types of redox reactions: Combination and decomposition, Displacement reactions (single and double), Combustion, Disproportionation. The oxidizing agent undergoes reduction and the reducing agent undergoes oxidation.

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20.2: Balanced Oxidation-Reduction Equations

Learning Objectives

- To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions. Most of the reactions we considered there were relatively simple, and balancing them was straightforward. When oxidation–reduction reactions occur in aqueous solution, however, the equations are more complex and can be more difficult to balance by inspection. Because a balanced chemical equation is the most important prerequisite for solving any stoichiometry problem, we need a method for balancing oxidation–reduction reactions in aqueous solution that is generally applicable. One such method uses *oxidation states*, and a second is referred to as the *half-reaction* method.

Balancing Redox Equations Using Oxidation States

To balance a redox equation using the oxidation state method, we conceptually separate the overall reaction into two parts: an oxidation—in which the atoms of one element lose electrons—and a reduction—in which the atoms of one element gain electrons. Consider, for example, the reaction of Cr^{2+}(aq) with manganese dioxide (MnO_2) in the presence of dilute acid. Equation 20.2.1 is the net ionic equation for this reaction before balancing; the oxidation state of each element in each species has been assigned using the procedure described previously (in red above each element):

$$\blacksquare(aq) + \overset{+4}{\mathrm{Mn}}\overset{-2}{\mathrm{O}}_2(aq) + \overset{+1}{\mathrm{H}^+}(aq) \rightarrow \blacksquare(aq) + \blacksquare(aq) + \overset{+1}{\mathrm{H}_2}\overset{-2}{\mathrm{O}}(l) \tag{20.2.1}$$

Notice that chromium is oxidized from the +2 to the +3 oxidation state, while manganese is reduced from the +4 to the +2 oxidation state. We can write an equation for this reaction that shows only the atoms that are oxidized and reduced (ignoring the oxygen and hydrogen atoms):

$$\mathrm{Cr}^{2+} + \mathrm{Mn}^{4+} \longrightarrow \mathrm{Cr}^{3+} + \mathrm{Mn}^{2+} \tag{20.2.2}$$

The oxidation can be written as

$$\underbrace{\mathrm{Cr}^{2+} \longrightarrow \mathrm{Cr}^{3+} + \mathrm{e}^-}_{\text{oxidation with 1 electron lost}} \tag{20.2.3}$$

and the reduction as

$$\underbrace{\mathrm{Mn}^{4+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Mn}^{2+}}_{\text{reduction with 2 electrons gained}} \tag{20.2.4}$$

For the overall chemical equation to be balanced, the number of electrons lost by the reductant must equal the number gained by the oxidant. We must therefore multiply the oxidation and the reduction equations by appropriate coefficients to give us the same number of electrons in both. In this example, we must multiply the oxidation (Equation 20.2.3) by 2 to give

$$2\,\mathrm{Cr}^{2+} \longrightarrow 2\,\mathrm{Cr}^{3+} + 2\,\mathrm{e}^- \tag{20.2.5}$$

The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction (Equation 20.2.4):

$$2\,\mathrm{Cr}^{2+} \rightarrow 2\,\mathrm{Cr}^{3+} + 2\,\mathrm{e}^-$$

$$\blacksquare + 2\,\mathrm{e}^- \rightarrow \blacksquare$$

We then add the equations for the oxidation and the reduction and cancel the electrons on both sides of the equation, using the actual chemical forms of the reactants and products:

$$2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + \cancel{2e^-}$$

$$\blacksquare + \cancel{2e^-} \rightarrow \blacksquare$$

to result in the balanced redox reaction (metals only)

$$Mn^{4+} + 2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + Mn^{2+} \tag{20.2.6}$$

now we can add the non-redox active atoms back into the equation (ignoring water and hydronium for now)

$$MnO_2\,(aq) + 2\,Cr^{2+}\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + Mn^{2+}\,(aq) \tag{20.2.7}$$

> In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of Equation 20.2.7 (+4) does not equal the charge on the right side (+8). Because the reaction is carried out in the presence of aqueous acid, we can add H^+ as necessary to either side of the equation to balance the charge. By the same token, if the reaction were carried out in the presence of aqueous base, we could balance the charge by adding OH^- as necessary to either side of the equation to balance the charges.

In this case, adding four H^+ ions to the left side of Equation 20.2.7 to give

$$MnO_2\,(s) + 2\,Cr^{2+}\,(aq) + 4\,H^+\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + Mn^{2+}\,(aq) \tag{20.2.8}$$

Although the charges are now balanced in Equation 20.2.8, we have two oxygen atoms on the left side of the equation and none on the right. We can balance the oxygen atoms without affecting the overall charge balance by adding H_2O as necessary to either side of the equation. Here, we need to add two H_2O molecules to the right side of Equation 20.2.8:

$$MnO_2\,(s) + 2\,Cr^{2+}\,(aq) + 4\,H^+\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + Mn^{2+}\,(aq) + 2\,H_2O\,(l) \tag{20.2.9}$$

Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced with respect to all atoms and charge. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized below and illustrated in Example 20.2.1 below.

Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method

1. Write the unbalanced chemical equation for the reaction, showing the reactants and the products.
2. Assign oxidation states to all atoms in the reactants and the products and determine which atoms change oxidation state.
3. Write separate equations for oxidation and reduction, showing (a) the atom(s) that is (are) oxidized and reduced and (b) the number of electrons accepted or donated by each.
4. Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.
5. Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in step 4.
6. Add the two equations and cancel the electrons.
7. Balance the charge by adding H^+ or OH^- ions as necessary for reactions in acidic or basic solution, respectively.
8. Balance the oxygen atoms by adding H_2O molecules to one side of the equation.
9. Check to make sure that the equation is balanced in both atoms and total charges.

Example 20.2.1: Balancing in Acid Solutions

Arsenic acid (H_3AsO_4) is a highly poisonous substance that was once used as a pesticide. The reaction of elemental zinc with arsenic acid in acidic solution yields arsine (AsH_3, a highly toxic and unstable gas) and $Zn^{2+}\,(aq)$. Balance the equation for this reaction using oxidation states:

$$H_3AsO_4\,(aq) + Zn\,(s) \longrightarrow AsH_3\,(g) + Zn^{2+}\,(aq)$$

Given: reactants and products in acidic solution

Asked for: balanced chemical equation using oxidation states

Strategy:

Follow the procedure given above for balancing a redox equation using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

1. *Write a chemical equation showing the reactants and the products.* Because we are given this information, we can skip this step.
2. *Assign oxidation states and determine which atoms change oxidation state.* The oxidation state of arsenic in arsenic acid is +5, and the oxidation state of arsenic in arsine is −3. Conversely, the oxidation state of zinc in elemental zinc is 0, and the oxidation state of zinc in $Zn^{2+}(aq)$ is +2:

$$\overset{+5}{H_3}\overset{}{A}\overset{}{s}\overset{}{O_4}(aq) + \overset{0}{Z}\overset{}{n}(s) \rightarrow \overset{-3}{A}\overset{}{s}\overset{}{H_3}(g) + \overset{+2}{Z}\overset{}{n}^{2+}(aq)$$

3. *Write separate equations for oxidation and reduction.* The arsenic atom in H_3AsO_4 is reduced from the +5 to the −3 oxidation state, which requires the addition of eight electrons:

$$\underbrace{\overset{+5}{A}\overset{}{s} + 8e^- \rightarrow \overset{-3}{A}\overset{}{s}}_{\text{Reduction with gain of 8 electrons}}$$

Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom:

$$\underbrace{\overset{0}{Z}\overset{}{n} \rightarrow \overset{+2}{Z}\overset{}{n}^{2+} + 2e^-}_{\text{Oxidation with loss of 2 electrons}}$$

4. *Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.* The reduction equation has eight electrons, and the oxidation equation has two electrons, so we need to multiply the oxidation equation by 4 to obtain

$$\begin{aligned} \overset{+5}{\mathrm{As}} + 8\,\mathrm{e}^- &\rightarrow \overset{-3}{\mathrm{As}} \\ 4\,\overset{0}{\mathrm{Zn}} &\rightarrow 4\,\overset{+2}{\mathrm{Zn}}^{2+} + 8\,\mathrm{e}^- \end{aligned}$$

5. *Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting coefficients as necessary to give the numbers of atoms shown in step 4.* Inserting the actual chemical forms of arsenic and zinc and adjusting the coefficients gives
   - Reduction:

$$\mathrm{H_3AsO_4\,(aq)} + 8\,\mathrm{e}^- \rightarrow \mathrm{AsH_3\,(g)}$$

   - Oxidation:

$$4\,\mathrm{Zn\,(s)} \longrightarrow 4\,\mathrm{Zn}^{2+}\,\mathrm{(aq)} + 8\,\mathrm{e}^-$$

6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is

$$\mathrm{H_3AsO_4\,(aq)} + 4\,\mathrm{Zn\,(s)} + \cancel{8\,\mathrm{e}^-} \rightarrow \mathrm{AsH_3\,(g)} + 4\,\mathrm{Zn}^{2+}\,\mathrm{(aq)} + \cancel{8\,\mathrm{e}^-}$$

which then yields after canceling electrons

$$\mathrm{H_3AsO_4\,(aq)} + 4\,\mathrm{Zn\,(s)} \rightarrow \mathrm{AsH_3\,(g)} + 4\,\mathrm{Zn}^{2+}\,\mathrm{(aq)}$$

7. *Balance the charge by adding H^+ or OH^- ions as necessary for reactions in acidic or basic solution, respectively.* Because the reaction is carried out in acidic solution, we can add H^+ ions to whichever side of the equation requires them to balance the charge. The overall charge on the left side is zero, and the total charge on the right side is 4 × (+2) = +8. Adding eight H^+ ions to the left side gives a charge of +8 on both sides of the equation:

$$\mathrm{H_3AsO_4\,(aq)} + 4\,\mathrm{Zn\,(s)} + 8\,\mathrm{H}^+\,\mathrm{(aq)} \rightarrow \mathrm{AsH_3\,(g)} + 4\,\mathrm{Zn}^{2+}\,\mathrm{(aq)}$$

8. *Balance the oxygen atoms by adding $\mathrm{H_2O}$ molecules to one side of the equation.* There are 4 O atoms on the left side of the equation. Adding 4 $\mathrm{H_2O}$ molecules to the right side balances the O atoms:

$$\mathrm{H_3AsO_4\,(aq) + 4\,Zn\,(s) + 8\,H^+\,(aq) \rightarrow AsH_3\,(g) + 4\,Zn^{2+}\,(aq) + 4\,H_2O\,(l)}$$

   Although we have not explicitly balanced H atoms, each side of the equation has 11 H atoms.
9. *Check to make sure that the equation is balanced in both atoms and total charges.* To guard against careless errors, it is important to check that both the total number of atoms of each element and the total charges are the same on both sides of the equation:
   - Atoms:

$$\mathrm{1\,As + 4\,Zn + 4\,O + 11\,H \overset{\checkmark}{=} 1\,As + 4\,Zn + 4\,O + 11\,H}$$

   - Charge:

$$8(+1) \overset{\checkmark}{=} 4(+2)$$

The balanced chemical equation (both for charge and for atoms) for this reaction is therefore:

$$\mathrm{H_3AsO_4\,(aq) + 4\,Zn\,(s) + 8\,H^+\,(aq) \longrightarrow AsH_3\,(g) + 4\,Zn^{2+}\,(aq) + 4\,H_2O\,(l)}$$

Exercise 20.2.1: Oxidizing Copper

Copper commonly occurs as the sulfide mineral CuS. The first step in extracting copper from CuS is to dissolve the mineral in nitric acid, which oxidizes the sulfide to sulfate and reduces nitric acid to NO. Balance the equation for this reaction using oxidation states:

$$\mathrm{CuS\,(s) + H^+\,(aq) + NO_3^-\,(aq) \longrightarrow Cu^{2+}\,(aq) + NO\,(g) + SO_4^{2-}\,(aq)}$$

Answer available at the end of this section.

Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example 20.2.2.

Example 20.2.2: Balancing in Basic Solution

The commercial solid drain cleaner, Drano, contains a mixture of sodium hydroxide and powdered aluminum. The sodium hydroxide dissolves in standing water to form a strongly basic solution, capable of slowly dissolving organic substances, such as hair, that may be clogging the drain. The aluminum dissolves in the strongly basic solution to produce bubbles of hydrogen gas that agitate the solution to help break up the clogs. The reaction is as follows:

$$\mathrm{Al\,(s) + H_2O\,(l) \rightarrow [Al(OH)_4]^-\,(aq) + H_2\,(g)}$$

Balance this equation using oxidation states.

Given: reactants and products in a basic solution

Asked for: balanced chemical equation

Strategy:

Follow the procedure given above for balancing a redox reaction using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

We will apply the same procedure used in Example 20.2.1, but in a more abbreviated form.

1. The equation for the reaction is given, so we can skip this step.

2. The oxidation state of aluminum changes from 0 in metallic Al to +3 in $[\mathrm{Al(OH)_4}]^-$. The oxidation state of hydrogen changes from +1 in $\mathrm{H_2O}$ to 0 in $\mathrm{H_2}$. Aluminum is oxidized, while hydrogen is reduced:

$$\overset{0}{Al}_{(s)} + \overset{+1}{H}_2O_{(aq)} \rightarrow [\overset{+3}{Al}(OH)_4]^-_{(aq)} + \overset{0}{H}_{2(g)}$$

3. Write separate equations for oxidation and reduction.
   - Reduction:

$$\overset{+1}{H} + e^- \rightarrow \overset{0}{H}\ (in\ H_2)$$

   - Oxidation:

$$\overset{0}{Al} \rightarrow \overset{+3}{Al} + 3e^-$$

4. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:
   - Reduction:

$$3\,\mathrm{H^+} + 3\,\mathrm{e^-} \longrightarrow 3\,\mathrm{H^0}\ (in\ \mathrm{H_2})$$

   - Oxidation:

$$\mathrm{Al^0} \longrightarrow \mathrm{Al^{3+}} + 3\,\mathrm{e^-}$$

5. Insert the actual chemical forms of the reactants and products, adjusting the coefficients as necessary to obtain the correct numbers of atoms as in step 4. Because a molecule of $\mathrm{H_2O}$ contains two protons, in this case, $3\,\mathrm{H^+}$ corresponds to $\frac{3}{2}\,\mathrm{H_2O}$. Similarly, each molecule of hydrogen gas contains two H atoms, so $3\,\mathrm{H}$ corresponds to $\frac{3}{2}\,\mathrm{H_2}$.
   - Reduction:

$$\tfrac{3}{2}\,\mathrm{H_2O} + 3\,\mathrm{e^-} \longrightarrow \tfrac{3}{2}\,\mathrm{H_2}$$

   - Oxidation:

$$\mathrm{Al} \longrightarrow [\mathrm{Al(OH)_4}]^- + 3\,\mathrm{e^-}$$

6. Adding the equations and canceling the electrons gives

$$\mathrm{Al} + \tfrac{3}{2}\,\mathrm{H_2O} + \cancel{3\,\mathrm{e^-}} \longrightarrow [\mathrm{Al(OH)_4}]^- + \tfrac{3}{2}\,\mathrm{H_2} + \cancel{3\,\mathrm{e^-}}$$

$$\mathrm{Al} + \tfrac{3}{2}\,\mathrm{H_2O} \longrightarrow [\mathrm{Al(OH)_4}]^- + \tfrac{3}{2}\,\mathrm{H_2}$$

   To remove the fractional coefficients, multiply both sides of the equation by 2:

$$2\,\mathrm{Al} + 3\,\mathrm{H_2O} \rightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

7. The right side of the equation has a total charge of –2, whereas the left side has a total charge of 0. Because the reaction is carried out in basic solution, we can balance the charge by adding two $\mathrm{OH^-}$ ions to the left side:

$$2\,\mathrm{Al} + 2\,\mathrm{OH^-} + 3\,\mathrm{H_2O} \longrightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

8. The left side of the equation contains five O atoms, and the right side contains eight O atoms. We can balance the O atoms by adding three H_2O molecules to the left side:

$$2\,\mathrm{Al} + 2\,\mathrm{OH^-} + 6\,\mathrm{H_2O} \longrightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

9. Be sure the equation is balanced:
   1. Atoms:

$$2\,\mathrm{Al} + 8\,\mathrm{O} + 14\,\mathrm{H} \overset{\checkmark}{=} 2\,\mathrm{Al} + 8\,\mathrm{O} + 14\,\mathrm{H}$$

   2. Charge:

$$(2)(0) + (2)(-1) + (6)(0) \overset{\checkmark}{=} (2)(-1) + (3)(0)$$

The balanced chemical equation is therefore

$$2\,\mathrm{Al\,(s)} + 2\,\mathrm{OH^-\,(aq)} + 6\,\mathrm{H_2O\,(l)} \rightarrow 2\,[\mathrm{Al(OH)_4}]^-\,\mathrm{(aq)} + 3\,\mathrm{H_2\,(g)}$$

Thus 3 mol of $\mathrm{H_2}$ gas are produced for every 2 mol of Al consumed.

Exercise 20.2.2: Reducing Manganese in permanganate

The permanganate ion reacts with nitrite ion in basic solution to produce manganese (IV) oxide and nitrate ion. Write a balanced chemical equation for the reaction.

Answer available at the end of this section.

As suggested in Examples 20.2.1 and 20.2.2, a wide variety of redox reactions are possible in aqueous solutions. The identity of the products obtained from a given set of reactants often depends on both the ratio of oxidant to reductant and whether the reaction is carried out in acidic or basic solution, which is one reason it can be difficult to predict the outcome of a reaction. Because oxidation–reduction reactions in solution are so common and so important, however, chemists have developed two general guidelines for predicting whether a redox reaction will occur and the identity of the products:

1. Compounds of elements in high oxidation states (such as ClO_4^-, NO_3^-, MnO_4^-, $Cr_2O_7^{2-}$, and UF_6) tend to act as *oxidants* and *become reduced* in chemical reactions.
2. Compounds of elements in low oxidation states (such as CH_4, NH_3, H_2S, and HI) tend to act as *reductants* and *become oxidized* in chemical reactions.

When an aqueous solution of a compound that contains an element in a high oxidation state is mixed with an aqueous solution of a compound that contains an element in a low oxidation state, an oxidation–reduction reaction is likely to occur.

> Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.

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Balancing a Redox Reaction in Acidic Conditions: Balancing a Redox Reaction in Acidic Conditions (opens in new window) [youtu.be]

Summary

Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation. In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation–reduction reactions in solution using the oxidation state method, in which the overall reaction is separated into an oxidation equation and a reduction equation.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 20.2.1: Oxidizing Copper

$$3\,CuS\,(s) + 8\,H^+\,(aq) + 8\,NO_3^-\,(aq) \rightarrow 3\,Cu^{2+}\,(aq) + 8\,NO\,(g) + 3\,SO_4^{2-}\,(aq) + 4\,H_2O\,(l)$$

Exercise 20.2.2: Reducing Manganese in permanganate

$$2\,MnO_4^-\,(aq) + 3\,NO_2^-\,(aq) + H_2O\,(l) \longrightarrow 2\,MnO_2\,(s) + 3\,NO_3^-\,(aq) + 2\,OH^-\,(aq)$$

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20.3: Voltaic Cells

Learning Objectives

- To understand the basics of voltaic cells
- To connect voltage from a voltaic cell to underlying redox chemistry

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two **half-reactions**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$\mathrm{Zn\,(s) + Br_2\,(aq)\ \rightarrow Zn^{2+}\,(aq) + 2\,Br^-\,(aq)}$$

The half-reactions are as follows:

reduction half-reaction:

$$\mathrm{Br_2\,(aq) + 2\,e^-\ \rightarrow 2\,Br^-\,(aq)}$$

oxidation half-reaction:

$$\mathrm{Zn\,(s)\ \rightarrow Zn^{2+}\,(aq) + 2\,e^-}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and $\mathrm{Br_2}$ is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation $20.3.1$). A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

> In any redox reaction, the number of electrons lost by the oxidation reaction(s) equals the number of electrons gained by the reduction reaction(s).

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A **galvanic (voltaic) cell** uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an **electrolytic cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure $20.3.1$). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining

the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.

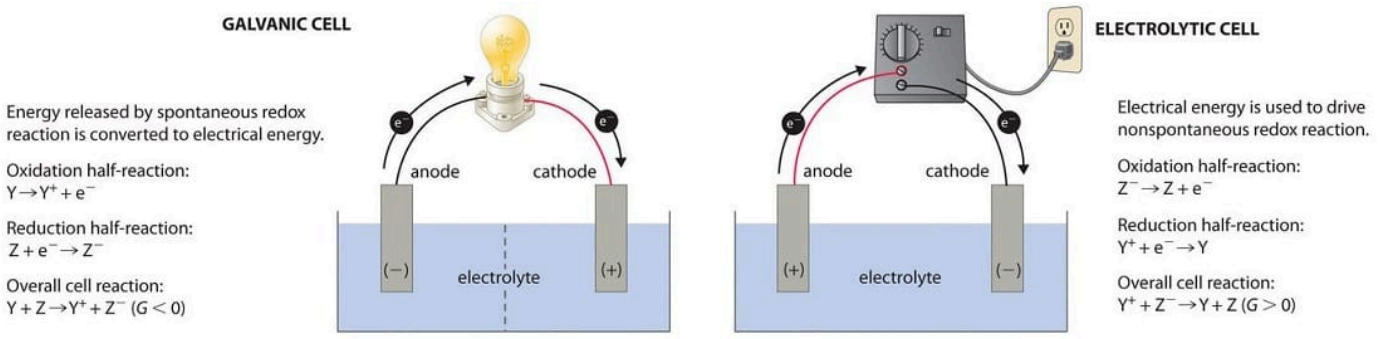


Figure 20.3.1: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Voltaic (Galvanic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$\mathrm{Zn\,(s) + Cu^{2+}\,(aq) \;\rightarrow Zn^{2+}\,(aq) + Cu\,(s)} \tag{20.3.1}$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.

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Figure 20.3.2: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $\mathrm{Zn^{2+}\,(aq)}$ ions, while $\mathrm{Cu^{2+}\,(aq)}$ ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. (youtu.be/2gPRK0HmYu4)

This same reaction can be carried out using the galvanic cell illustrated in Figure 20.3.3*a*. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of $\mathrm{Cu^{2+}}$ ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of $\mathrm{Zn^{2+}}$ ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a **salt bridge**, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are $\mathrm{Na^+}$ or $\mathrm{K^+}$ and $\mathrm{NO_3^-}$ or $\mathrm{SO_4^{2-}}$, respectively. (The ions in the salt bridge do not have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to $\mathrm{Zn^{2+}}$ ions at the zinc electrode (the anode),

and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the solution decreases (Figure $20.3.3b$). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

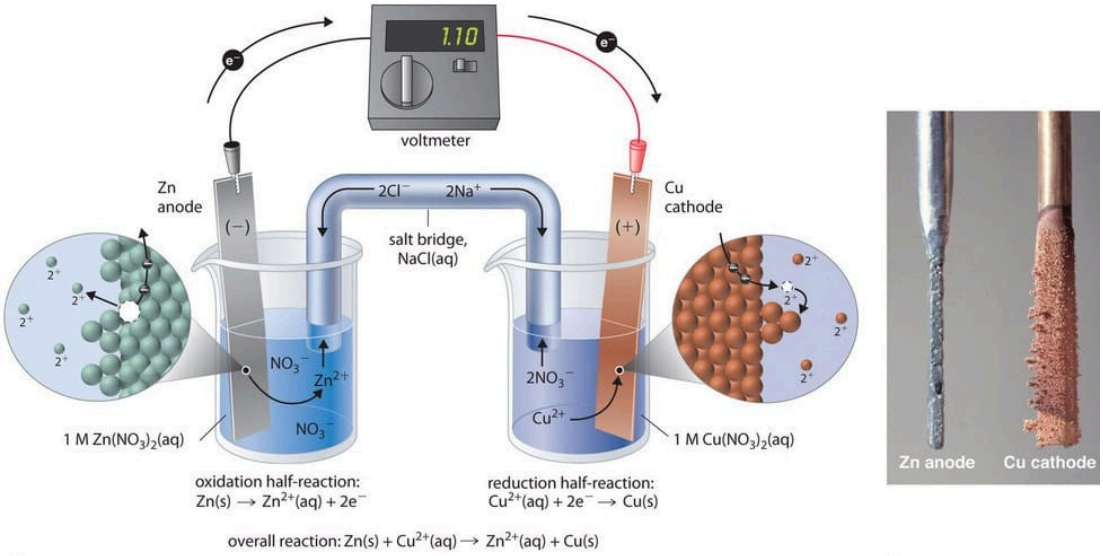


Figure $20.3.3$: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give Zn^{2+}(aq) ions, while the Cu cathode gains mass as Cu^{2+}(aq) ions are reduced to copper metal that is deposited on the cathode. (CC BY-SA-NC; anonymous)

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The **potential** (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (Figure $20.3.3a$). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example $20.3.1$.

A galvanic (voltaic) cell converts the energy released by a **spontaneous** chemical reaction to electrical energy. An

electrolytic cell consumes electrical energy from an external source to drive a **nonspontaneous** chemical reaction.

Example 20.3.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3\,\mathrm{Sn\,(s)} + 2\,\mathrm{NO_3{}^-\,(aq)} + 8\,\mathrm{H^+\,(aq)} \rightarrow 3\,\mathrm{Sn^{2+}\,(aq)} + 2\,\mathrm{NO\,(g)} + 4\,\mathrm{H_2O\,(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A. Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.
B. From the direction of electron flow, assign each electrode as either positive or negative.

Solution

A In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction:

$$\mathrm{NO_3{}^-\,(aq)} + 4\,\mathrm{H^+\,(aq)} + 3\,\mathrm{e^-} \longrightarrow \mathrm{NO\,(g)} + 2\,\mathrm{H_2O\,(l)}$$

oxidation:

$$\mathrm{Sn\,(s)} \longrightarrow \mathrm{Sn^{2+}\,(aq)} + 2\,\mathrm{e^-}$$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

B Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow from the tin electrode, it must be electrically negative. In contrast, electrons flow toward the Pt electrode, so that electrode must be electrically positive.

Exercise 20.3.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of $\mathrm{MnO_4{}^-}$ in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of $\mathrm{Sn^{2+}}$ in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2\,MnO_4^-\,(aq) + 5\,Sn^{2+}\,(aq) + 16\,H^+\,(aq) \rightarrow 2\,Mn^{2+}\,(aq) + 5\,Sn^{4+}\,(aq) + 8\,H_2O\,(l)$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is positive and which is negative.

Answer a available at the end of this section.

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Constructing Cell Diagrams (Cell Notation)

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a cell diagram, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the Zn/Cu cell shown in Figure $20.3.3a$ is written as follows:

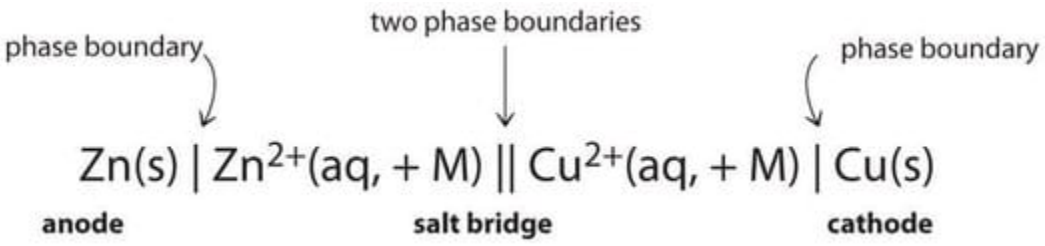


Figure $20.3.4$: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

At the anode is solid zinc. after the phase boundary is aq Zinc two plus and plus M. After the two phase boundary is aq copper two plus and plus M. At the cathode is solid copper.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the **junction potential**. One example of this type of galvanic cell is as follows:

$$Pt(s)\ |\ H_2\,(g)\ |\ HCl(aq,\ 1\,M)\ |\ AgCl\,(s)\ Ag\,(s)$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

cathode reaction:

$$AgCl\,(s) + e^- \rightarrow Ag\,(s) + Cl^-\,(aq)$$

anode reaction:

$$\tfrac{1}{2}\,\mathrm{H_2\,(g)} \longrightarrow \mathrm{H^+\,(aq)} + \mathrm{e^-}$$

overall:

$$\mathrm{AgCl\,(s)} + \tfrac{1}{2}\,\mathrm{H_2\,(g)} \longrightarrow \mathrm{Ag\,(s)} + \mathrm{Cl^-} + \mathrm{H^+\,(aq)}$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

Example 20.3.2

Draw a cell diagram for the galvanic cell described in Example 20.3.1. The balanced chemical reaction is as follows:

$$3\,\mathrm{Sn\,(s)} + 2\,\mathrm{NO_3^-\,(aq)} + 8\,\mathrm{H^+\,(aq)} \rightarrow 3\,\mathrm{Sn^{2+}\,(aq)} + 2\,\mathrm{NO\,(g)} + 4\,\mathrm{H_2O\,(l)}$$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $\mathrm{Sn(s)\,|\,Sn^{2+}\,(aq)}$. We could include $\mathrm{H_2SO_4\,(aq)}$ with the contents of the anode compartment, but the sulfate ion (as $\mathrm{HSO_4^-}$) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $\mathrm{HNO_3(aq)\,|\,NO(g)\,|\,Pt\,(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$\mathrm{Sn(s)\,|\,Sn^{2+}(aq)\,||\,HNO_3(aq)\,|\,NO(g)\,|\,Pt_{(}s)}$$

The solution concentrations were not specified, so they are not included in this cell diagram.

Exercise 20.3.2

Draw the cell diagram for the following reaction, assuming the concentration of $\mathrm{Ag^+}$ and $\mathrm{Mg^{2+}}$ are each 1 M:

$$\mathrm{Mg\,(s)} + 2\,\mathrm{Ag^+\,(aq)} \rightarrow \mathrm{Mg^{2+}\,(aq)} + 2\,\mathrm{Ag\,(s)}$$

Answer available at the end of this section.

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Summary

A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur. Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. An electric current is produced from the flow of electrons from the reductant to the oxidant. An electrochemical cell can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a galvanic (voltaic) cell, the energy from a spontaneous reaction generates electricity, whereas in an electrolytic cell, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two electrodes that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the anode, and the reductive half-reaction occurs at the cathode. A salt bridge connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The potential of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

Answers

Exercise 20.3.1

$$\mathrm{MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)}$$

$$\mathrm{Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\,e^-}$$

The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.

Exercise 20.3.2

$$\mathrm{Mg(s)\ |Mg^{2+}(aq,\ 1\ M\ )||\,Ag^{+}(aq,\ 1\ \ M)\,|\,Ag(s)}$$

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20.4: Cell Potential Under Standard Conditions

Learning Objectives

- To use redox potentials to predict whether a reaction is spontaneous.
- To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the s electrons of zinc by the electrons in filled d orbitals. Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper. Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

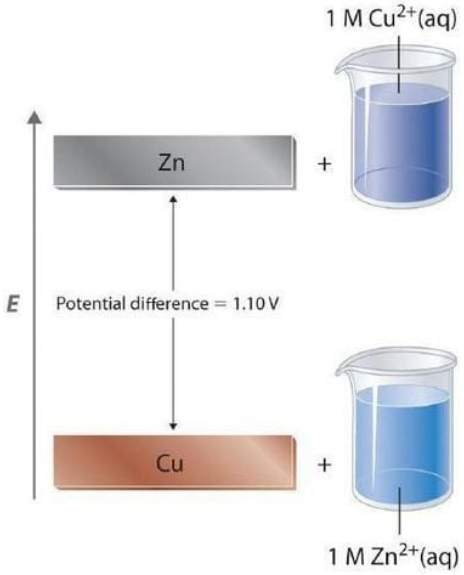


Figure 20.4.1: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic Zn and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous Zn^{2+} ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure 20.4.1 but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an activity of 1 rather than a concentration of 1 M. Corrections for non ideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured (this is analogous to measuring **absolute enthalpies** or **free energies**; recall that only differences in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential (E°) for the Zn/Cu system is 1.10 V, whereas E° for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V – 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co_{(s)} \mid Co^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E°= 0.59\ V \tag{20.4.1}$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances (Table P1). The standard cell potential ($E°_{cell}$) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E°_{cell} = E°_{cathode} - E°_{anode} \tag{20.4.2}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the sum of the two half-reactions. According to Equation 20.4.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

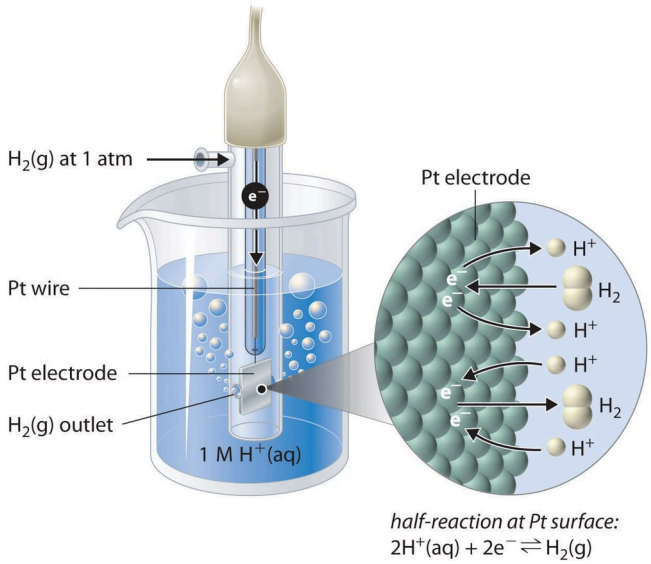


Figure 20.4.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 20.4.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{20.4.3}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

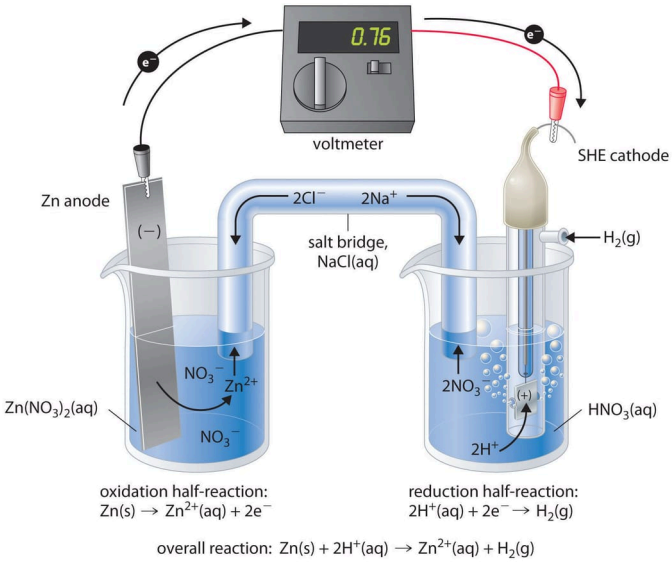


Figure 20.4.3: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form $Zn^{2+}(aq)$ ions while $H^+(aq)$ ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Figure 20.4.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel H^+(aq, 1M) \mid H_2(g, 1atm) \mid Pt_{(s)} \tag{20.4.4}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E°_{cathode} = 0V \tag{20.4.5}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E°_{anode} = -0.76\ V \tag{20.4.6}$$

- overall:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{20.4.7}$$

We then use Equation 20.4.2 to calculate the cell potential

$$\begin{aligned} E°_{cell} &= E°_{cathode} - E°_{anode} \\ &= 0.76\ V \end{aligned}$$

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction. In this example, the standard reduction potential for $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the Zn/Zn^{2+} redox couple, or the Zn/Zn^{2+} couple, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain

$$E°_{cell} : 0\,V - (-0.76\,V) = 0.76\,V$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

E° values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.

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The Standard Hydrogen Electrode (SHE): The Standard Hydrogen Electrode (SHE)(opens in new window) [youtu.be]

Standard Electrode Potentials

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure 20.4.3 but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (–0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt_{(s)} \mid H_2(g, 1atm) \mid H^+(aq, 1\ M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{20.4.8}$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu_{(g)} \quad E°_{cathode} = 0.34\ V \tag{20.4.9}$$

- Anode:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \quad E°_{anode} = 0\ V \tag{20.4.10}$$

- Overall:

$$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)} \tag{20.4.11}$$

We then use Equation 20.4.2 to calculate the cell potential

$$\begin{aligned} E°_{cell} &= E°_{cathode} - E°_{anode} \\ &= 0.34\ V \end{aligned}$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

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Balancing Redox Reactions Using the Half-Reaction Method

In Section 4.4, we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:

$$Al_{(s)} + OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + H_{2(g)} \tag{20.4.12}$$

In this reaction, $Al_{(s)}$ is oxidized to Al^{3+}, and H^+ in water is reduced to H_2 gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed Table P1, we find the corresponding half-reactions that describe the reduction of H^+ ions in water to $H_2$and the oxidation of Al to Al^{3+} in basic solution:

- reduction:

$$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)} \tag{20.4.13}$$

- oxidation:

$$Al_{(s)} + 4OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + 3e^- \tag{20.4.14}$$

The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In Equation 20.4.13, two H^+ ions gain one electron each in the reduction; in Equation 20.4.14, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 20.4.13) by 3 and the oxidation half-reaction (Equation 20.4.14) by 2 to give the same number of electrons in both half-reactions:

- reduction:

$$6H_2O_{(l)} + 6e^- \rightarrow 6OH^-_{(aq)} + 3H_{2(g)} \tag{20.4.15}$$

- oxidation:

$$2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 6e^- \tag{20.4.16}$$

Adding the two half-reactions,

$$6H_2O_{(l)} + 2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-4(aq) + 3H_{2(g)} + 6OH^-_{(aq)} \tag{20.4.17}$$

Simplifying by canceling substances that appear on both sides of the equation,

$$6H_2O_{(l)} + 2Al_{(s)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{20.4.18}$$

We have a –2 charge on the left side of the equation and a –2 charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:

$$2Al + 8O + 14H = 2Al + 8O + 14H \tag{20.4.19}$$

The atoms also balance, so Equation 20.4.18 is a balanced chemical equation for the redox reaction depicted in Equation 20.4.12.

> The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Table P1, but instead focus on the atoms whose oxidation states change, as illustrated in the following steps:

Step 1: Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 20.4.12, hydrogen is reduced from H^+ in OH^- to H_2, and aluminum is oxidized from Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} \tag{20.4.20}$$

- oxidation:

$$Al_{(s)} \rightarrow Al(OH)^-_{4(aq)} \tag{20.4.21}$$

Step 2: Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding H_2O and balance H atoms by adding H^+.

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{20.4.22}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} \tag{20.4.23}$$

Balancing H atoms by adding H^+, we obtain the following:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{20.4.24}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} \tag{20.4.25}$$

We have now balanced the atoms in each half-reaction, but the charges are not balanced.

Step 3: Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of H^+ ions to H_2, and three electrons are lost during the oxidation of Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} + H_2O_{(l)} \tag{20.4.26}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} + 3e^- \tag{20.4.27}$$

Step 4: Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 20.4.26 (the reductive half-reaction) by 3 and Equation 20.4.27 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

- reduction:

$$3OH^-_{(aq)} + 9H^+_{(aq)} + 6e^- \rightarrow 3H_{2(g)} + 3H_2O_{(l)} \tag{20.4.28}$$

- oxidation:

$$2Al_{(s)} + 8H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} + 8H^+_{(aq)} + 6e^- \tag{20.4.29}$$

Step 5: Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling $8H^+$, $3H_2O$, and $6e^-$,

$$2Al_{(s)} + 5H_2O_{(l)} + 3OH^-_{(aq)} + H^+_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{20.4.30}$$

We have three OH^- and one H^+ on the left side. Neutralizing the H^+ gives us a total of $5H_2O + H_2O = 6H_2O$ and leaves $2OH^-$ on the left side:

$$2Al_{(s)} + 6H_2O_{(l)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{20.4.31}$$

Step 6: Check to make sure that all atoms and charges are balanced.

Equation 20.4.31 is identical to Equation 20.4.18, obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

Example 20.4.1

In acidic solution, the redox reaction of dichromate ion ($Cr_2O_7^{2-}$) and iodide (I^-) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green $Cr^{3+}(aq)$ complex and brown $I_2(aq)$ ions (Figure 20.4.4):

$$Cr_2O_7^{2-}(aq) + I^-(aq) \longrightarrow Cr^{3+}(aq) + I_2(aq)$$

Balance this equation using half-reactions.

Given: redox reaction and Table P1

Asked for: balanced chemical equation using half-reactions

Strategy:

Follow the steps to balance the redox reaction using the half-reaction method.

Solution

From the standard electrode potentials listed in Table P1, we find the half-reactions corresponding to the overall reaction:

- reduction:

$$\mathrm{Cr_2O_7}^{2-}\,(\mathrm{aq}) + 14\,\mathrm{H}^+\,(\mathrm{aq}) + 6\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Cr}^{3+}\,(\mathrm{aq}) + 7\,\mathrm{H_2O}\,(\mathrm{l})$$

- oxidation:

$$2\,\mathrm{I}^-\,(\mathrm{aq}) \longrightarrow \mathrm{I_2}\,(\mathrm{aq}) + 2\,\mathrm{e}^-$$

Balancing the number of electrons by multiplying the oxidation reaction by 3,

- oxidation:

$$6\,\mathrm{I}^-\,(\mathrm{aq}) \longrightarrow 3\,\mathrm{I_2}\,(\mathrm{aq}) + 6\,\mathrm{e}^-$$

Adding the two half-reactions and canceling electrons,

$$\mathrm{Cr_2O_7^{2-}}\,(\mathrm{aq}) + 14\,\mathrm{H}^+\,(\mathrm{aq}) + 6\,\mathrm{I}^-\,(\mathrm{aq}) \longrightarrow 2\,\mathrm{Cr}^{3+}\,(\mathrm{aq}) + 7\,\mathrm{H_2O}\,(\mathrm{l}) + 3\,\mathrm{I_2}\,(\mathrm{aq})$$

We must now check to make sure the charges and atoms on each side of the equation balance:

$$(-2) + 14 + (-6) = +6$$

$$+6 \overset{\checkmark}{=} +6$$

and atoms

$$2\,\mathrm{Cr} + 7\,\mathrm{O} + 14\,\mathrm{H} + 6\,\mathrm{I} \overset{\checkmark}{=} 2\,\mathrm{Cr} + 7\,\mathrm{O} + 14\,\mathrm{H} + 6\,\mathrm{I}$$

Both the charges and atoms balance, so our equation is balanced.

We can also use the alternative procedure, which does not require the half-reactions listed in Table P1.

Step 1: Chromium is reduced from Cr^{6+} in $\mathrm{Cr_2O_7}^{2-}$ to Cr^{3+}, and I^- ions are oxidized to $\mathrm{I_2}$. Dividing the reaction into two half-reactions,

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow Cr^{3+}_{(aq)}$$

- oxidation:

$$I^-_{(aq)} \rightarrow I_{2(aq)}$$

Step 2: Balancing the atoms other than oxygen and hydrogen,

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow 2Cr^{3+}_{(aq)}$$

- oxidation:

$$2I^-_{(aq)} \rightarrow I_{2(aq)}$$

We now balance the O atoms by adding H_2O—in this case, to the right side of the reduction half-reaction. Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

Next we balance the H atoms by adding H^+ to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

- reduction:

$$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

Step 3: We must now add electrons to balance the charges. The reduction half-reaction ($2Cr^{+6}$ to $2Cr^{+3}$) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ($2I^-$ to I_2) has a –2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

- reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
- oxidation: $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Step 4: To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:

- oxidation: $6I^-(aq) \rightarrow 3I_2(s) + 6e^-$

Step 5: Adding the two half-reactions and canceling substances that appear in both reactions,

$$\mathrm{Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) + 6\,I^-\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l) + 3\,I_2\,(aq)}$$

Step 6: This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

Exercise 20.4.1

Copper is found as the mineral covellite (CuS). The first step in extracting the copper is to dissolve the mineral in nitric acid ($\mathrm{HNO_3}$), which oxidizes sulfide to sulfate and reduces nitric acid to NO:

$$\mathrm{CuS\,(s) + HNO_3\,(aq) \rightarrow NO\,(g) + CuSO_4\,(aq)}$$

Balance this equation using the half-reaction method.



Covellite (also known as covelline) is a rare copper sulfide mineral with an indigo blue color that is ubiquitous in copper ores. (CC SA-BY 3.0;'Didier Descouens).

Answer available at the end of this section.

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{20.4.32}$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E°_{cell}$:

- cathode:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E°_{cathode} = 0.34\ V \tag{20.4.33}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}(aq, 1M) + 2e^- \qquad E°_{anode} = -0.76\ V \tag{20.4.34}$$

- overall:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{20.4.35}$$

$$E°_{cell} = E°_{cathode} - E°_{anode} = 1.10\ V$$

This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see in Section 20.9, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example 20.4.2 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

> A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.

Example 20.4.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

anode: $Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A. Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.
B. Use Equation 20.4.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

B Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 20.4.2:

$$\begin{aligned} E°_{cell} &= E°_{cathode} - E°_{anode} \\ 0.27\,V &= E°°_{cathhode} - (-0.55\,V) \\ E°_{cathode} &= -0.28\,V \end{aligned}$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus $E° = -(-0.28\text{ V}) = 0.28$ V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

Exercise 20.4.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $\mathrm{Hg(CH_3CO_2)_2}$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $\mathrm{MgCl_2}$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode: $\mathrm{Hg^{2+}\,(aq) + 2\,e^- \longrightarrow Hg\,(l)}$
- anode: $\mathrm{Mg\,(s) \longrightarrow Mg^{2+}\,(aq) + 2\,e^-}$

If the potential for the oxidation of Mg to $\mathrm{Mg^{2+}}$ is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the cathode?

Answer available at the end of this section.

Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called **indicator electrode**, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the **reference electrode**, must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

> The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference

electrodes. One is the **silver–silver chloride electrode**, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

$$Cl^-_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)} \tag{20.4.36}$$

$$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the **saturated calomel electrode (SCE)**, which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called calomel in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure 20.4.5. Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$Pt_{(s)} \mid Hg_2Cl_{2(s)} \mid KCl_{(aq,sat)} \tag{20.4.37}$$

$$Hg_2Cl_{2(s)} + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-(aq) \tag{20.4.38}$$

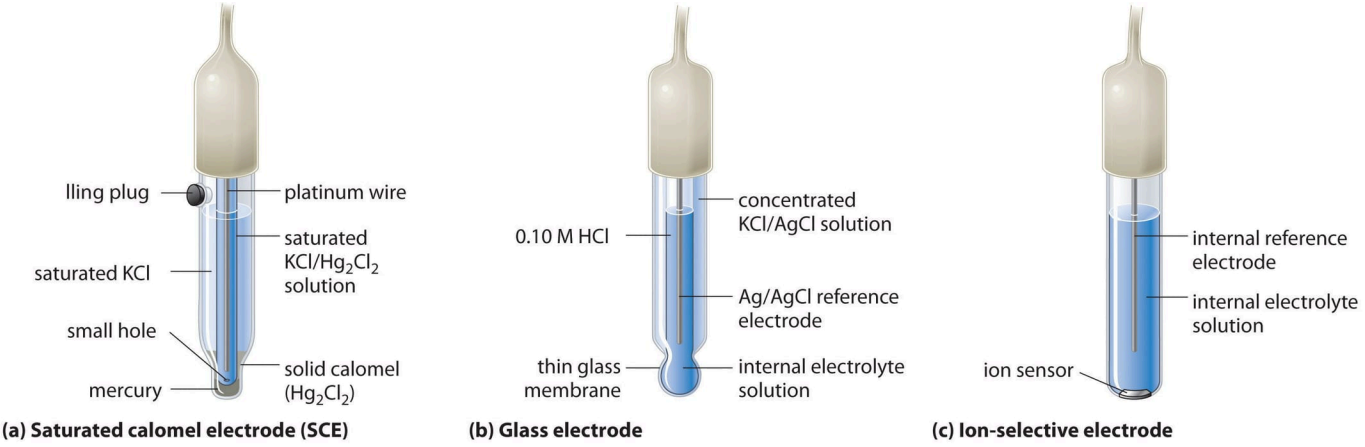


Figure 20.4.5: Three Common Types of Electrodes. (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution. (CC BY-SA-NC; anonymous)

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A **glass electrode** is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure 20.4.5. The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because [H^+] is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on [H^+] as follows (recall that pH = –log[H^+]):

$$E_{glass} = E' + (0.0591\ V \times \log[H^+]) = E' - 0.0591\ V \times pH \tag{20.4.39}$$

The voltage E′ is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is calibrated; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodes are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure 20.4.5). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called fluoride electrode. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 20.4.1.

Table 20.4.1: Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

Redox reactions can be balanced using the half-reaction method. The standard cell potential is a measure of the driving force for the reaction. \(E°_{cell} = E°_{cathode} – E°_{anode} \nonumber \] The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the standard cell potential ($E°_{cell}$). Only the difference between the potentials of two electrodes can be measured. By convention, all tabulated values of standard electrode potentials are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} – E°_{anode}$). The potential of the standard hydrogen electrode (SHE) is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its standard electrode potential. The standard cell potential is a measure of the driving force for a given redox reaction. All E° values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of E° corresponding to that reaction must also be reversed. If $E°_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E°_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an indicator electrode is related to the concentration of the substance being measured, whereas the potential of the reference electrode is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the silver–silver chloride electrode; the saturated calomel electrode (SCE); the glass electrode, which is commonly used to measure pH; and ion-selective electrodes, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for E°.

Answers

Exercise 20.4.1

$$3\,\mathrm{CuS\,(s)} + 8\,\mathrm{HNO_3\,(aq)} \longrightarrow 8\,\mathrm{NO\,(g)} + 3\,\mathrm{CuSO_4\,(aq)} + 4\,\mathrm{H_2O\,(l)}$$

Exercise 20.4.2

0.85 V

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20.5: Gibbs Energy and Redox Reactions

Learning Objectives

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of $\mathrm{Co(s)}$ with $\mathrm{Ni^{2+}(aq)}$ to form $\mathrm{Ni(s)}$ and $\mathrm{Co^{2+}(aq)}$ occurs spontaneously, but if we reduce the concentration of $\mathrm{Ni^{2+}}$ by a factor of 100, so that $[\mathrm{Ni^{2+}}]$ is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential & Gibbs Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction.

The resulting electric current involves the movement of an electric charge measured in coulombs (C), an SI unit that has been defined, since 2019, to give an electron a charge of exactly $1.602176634\times10^{-19}$ C. This means that a coulomb is the electric charge carried by about $6.241\,509 \times 10^{18}$ electrons. Electric current is measured in **amperes (A)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s). Voltage is the potential difference required to move a charge through a circuit. By definition a coulomb of charge flowing through a potential difference of 1 V will require a 1J of energy

$$\frac{1\ J}{1\ V} = 1\ C$$

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$\begin{aligned} F &= (1.60218 \times 10^{-19}\ \mathrm{C}) \left(\frac{6.02214 \times 10^{23}\ J}{1\ \mathrm{mol\ e^-}} \right) \\ &= 9.64833212 \times 10^{4}\ \mathrm{C/mol\ e^-} \\ &\simeq 96,485\, C/(\mathrm{mol\ e^-}) \end{aligned}$$

The total charge transferred from the reductant to the oxidant is therefore nF, where n is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{20.5.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of $E°_{cell}$.

Example 20.5.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table P2, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG^o for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E^o, write the overall reaction and calculate E°_{cell}.
B. Determine the number of electrons transferred in the overall reaction. Then use Equation 20.5.1 to calculate ΔG^o. If ΔG^o is negative, then the reaction is spontaneous.

Solution

A

As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E^o. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E^o values:

$$\begin{array}{lll} \text{cathode:} & \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} & E^\circ_{\text{cathode}} = 1.36\ \text{V} \\ \text{anode:} & \mathrm{2Br^-(aq) \rightarrow Br_2(aq) + 2e^-} & E^\circ_{\text{anode}} = 1.09\ \text{V} \end{array}$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of E^o is not affected:

$$\begin{array}{lll} \text{cathode:} & \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} & E^\circ_{\text{cathode}} = 1.36\ \text{V} \\ \text{anode:} & \mathrm{6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-} & E^\circ_{\text{anode}} = 1.09\ \text{V} \\ \text{overall:} & \mathrm{Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)} & E^\circ_{\text{cell}} = 0.27\ \text{V} \end{array}$$

B

We can now calculate ΔG° using Equation 20.5.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned}\Delta G^\circ &= -(n)(F)(E^\circ_{\text{cell}}) \\ &= -(6\text{ mole})[96,485\text{ J/(V}\cdot\text{mol})(0.27\text{ V})] \\ &= -15.6\times 10^4\text{ J} \\ &= -156\text{ kJ/mol }\text{Cr}_2\text{O}_7^{2-}\end{aligned}$$

Thus ΔG^o is –168 kJ/mol for the reaction as written, and the reaction is spontaneous.

Exercise 20.5.1

Use the data in Table P2 to calculate ΔG^o for the reduction of ferric ion by iodide:

$$2\,\text{Fe}^{3+}\,(\text{aq}) + 2\,\text{I}^-\,(\text{aq}) \longrightarrow 2\,\text{Fe}^{2+}\,(\text{aq}) + \text{I}_2\,(\text{s})$$

Is the reaction spontaneous?

Answer available at the end of this section.

Potentials for the Sums of Half-Reactions

Although Table P2 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of $\text{Fe}^{3+}\,(\text{aq})$ to $\text{Fe}\,(\text{s})$ is not listed in the table, but two related reductions are given:

$$\text{Fe}^{3+}\,(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}\,(\text{aq}) \quad E^\circ = +0.77V$$

$$\text{Fe}^{2+}\,(\text{aq}) + 2\,\text{e}^- \longrightarrow \text{Fe}\,(\text{s}) \quad E^\circ = -0.45V$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction because E^o is not a state function. However, because ΔG^o is a state function, the sum of the ΔG^o values for the individual reactions gives us ΔG^o for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E^o for the overall half-reaction, we first must add the values of $\Delta G^o(\,=-nFE^o)$ for each individual half-reaction to obtain ΔG^o for the overall half-reaction:

$$\begin{aligned}\text{Fe}^{3+}\,(\text{aq}) + \text{e}^- &\rightarrow \text{Fe}^{2+}\,(\text{aq}) & \Delta G^\circ &= -(1)(F)(0.77\text{ V}) \\ \text{Fe}^{2+}\,(\text{aq}) + 2\,\text{e}^- &\rightarrow \text{Fe}\,(\text{s}) & \Delta G^\circ &= -(2)(F)(-0.45\text{ V}) \\ \text{Fe}^{3+}\,(\text{aq}) + 3\,\text{e}^- &\rightarrow \text{Fe}\,(\text{s}) & \Delta G^\circ &= [-(1)(F)(0.77\text{ V})] + [-(2)(F)(-0.45\text{ V})]\end{aligned}$$

Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^\circ = F\,[(-0.77V) + (-2)(-0.45V)] = F(0.13V)$$

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 20.5.1 and solving for E^o gives the following:

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ F(0.13\text{ V}) &= -(3)(F)(E^\circ_{\text{cell}}) \\ E^\circ &= -\frac{0.13\text{ V}}{3} = -0.043\text{ V}\end{aligned}$$

This value of E^o is very different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

> Values of E^o for half-reactions cannot be added to give E^o for the sum of the half-reactions; only values of $\Delta G^o = -nFE^\circ_{cell}$ for half-reactions can be added.

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^\circ = -RT \ln K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 20.5.1), we can write

$$-nFE^\circ_{cell} = -RT \ln K$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{20.5.2}$$

For $T = 298\ K$, Equation 20.5.2 can be simplified as follows:

$$\begin{aligned} E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right) \ln K \\ &= \left[\frac{[8.314\ \text{J/(mol} \cdot \text{K)(298 K)}]}{n[96,485\ \text{J/(V} \cdot \text{mol)}]}\right] 2.303 \log K \\ &= \left(\frac{0.0592\ \text{V}}{n}\right) \log K \end{aligned} \tag{20.5.3}$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

Example 20.5.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E^o_{cell}.
B. Determine the number of electrons transferred in the overall reaction. Use Equation 20.5.3 to solve for $\log K$ and then K.

Solution

A The relevant half-reactions and potentials from Table P2 are as follows:

cathode:	$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	$E^\circ_{\text{cathode}} = 1.69\ \text{V}$
anode:	$\text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$	$E^\circ_{\text{anode}} = -0.36\ \text{V}$
overall:	$\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	$E^\circ_{\text{cell}} = 2.05\ \text{V}$

B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 20.5.3 for log K and inserting the values of n and E^o,

$$\log K = \frac{nE^\circ}{0.0591\ \text{V}} = \frac{2(2.05\ \text{V})}{0.0591\ \text{V}} = 69.37$$

$$K = 2.3 \times 10^{69}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

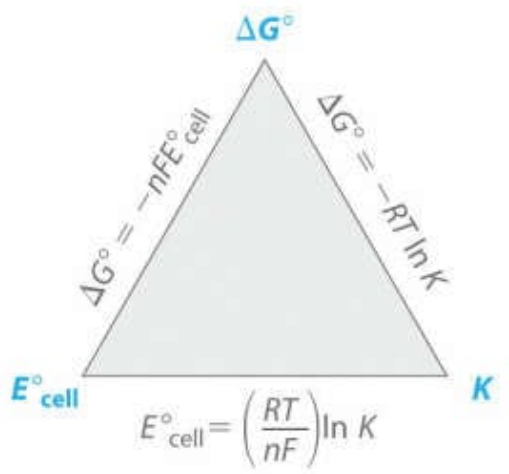
Exercise 20.5.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of $\text{Sn}^{2+}\,(\text{aq})$ with oxygen to produce $\text{Sn}^{4+}\,(\text{aq})$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2\,\text{Sn}^{2+}\,(\text{aq}) + \text{O}_2\,(\text{g}) + 4\,\text{H}^+\,(\text{aq}) \rightleftharpoons 2\,\text{Sn}^{4+}\,(\text{aq}) + 2\,\text{H}_2\text{O}\,(\text{l})$$

Answer available at the end of this section.

Figure 20.5.1 summarizes the relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity (ΔG° < 0). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q.



ΔG°	E°_{cell}	K	Direction of Reaction
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure 20.5.1: The Relationships among Criteria for Thermodynamic Spontaneity. The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, ΔG°, and E°_{cell}. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of ΔG° and E°_{cell} and the magnitude of K determine the direction of spontaneous reaction under standard conditions. (CC BY-NC-SA; Anonymous by request)

If ΔG is less than zero, E^o is greater than zero and K is greater than 1 then the direction of the reaction is spontaneous in forward direction. If ΔG is greater than zero, E^o is less than zero and K is less than one then the direction of reaction is spontaneous in reverse direction. If ΔG is zero, E is zero and K is one that there is no net reaction and the system is at equilibrium .

Summary

A coulomb (C) relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in amperes (A), where 1 A is defined as the flow of 1 C/s past a given point. The faraday (F) is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, E°_{cell} and K are also

related. Large equilibrium constants correspond to large positive values of E°.

Answers

Exercise 20.5.1

−44 kJ/mol I_2; yes

Exercise 20.5.2

5.7×10^{72}

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20.6: Cell Potential Under Nonstandard Conditions

Learning Objectives

- Relate cell potentials to Gibbs energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall that the actual free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G° + RT \ln Q \tag{20.6.1}$$

We also know that $\Delta G = -nFE_{cell}$ (under non-standard conditions) and $\Delta G^o = -nFE^o_{cell}$ (under standard conditions). Substituting these expressions into Equation 20.6.1, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT \ln Q \tag{20.6.2}$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q \tag{20.6.3}$$

Equation 20.6.3 is called the **Nernst equation**, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), then Equation 20.6.3 reduces to Equation 20.6.4 and 20.6.5 because $Q = K$, and there is no net transfer of electrons (i.e., $E_{cell} = 0$).

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln K = 0 \tag{20.6.4}$$

since

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{20.6.5}$$

Substituting the values of the constants into Equation 20.6.3 with $T = 298\ K$ and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential ($E°_{cell}$), and the reactant and product concentrations at room temperature (contained in Q):

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{20.6.6}$$

The Power of the Nernst Equation

The Nernst Equation (20.6.3) can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 20.6.6 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox

reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 20.6.6 that the cell potential changes by 0.0591/n V for each 10-fold change in the value of Q because log 10 = 1.

Example 20.6.1

The following reaction proceeds spontaneously under standard conditions because E°$_{cell}$ > 0 (which means that ΔG° < 0):

$$2\,Ce^{4+}\,(aq) + 2\,Cl^{-}\,(aq) \longrightarrow 2\,Ce^{3+}\,(aq) + Cl_2\,(g) \qquad E^{\circ}_{cell} = 0.25\,V$$

Calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: [Ce^{4+}] = 0.013 M, [Ce^{3+}] = 0.60 M, [Cl^-] = 0.0030 M, P_{Cl_2} = 1.0 atm, and T = 25°C.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 20.6.6 instead of Equation 20.6.3. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}_{(aq)} + 2e^{-} \rightarrow 2Ce^{3+}_{(aq)}$$

$$2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl_2, and the value of E°$_{cell}$ into Equation 20.6.6,

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0.25\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{[\text{Ce}^{3+}]^2 P_{\text{Cl}_2}}{[\text{Ce}^{4+}]^2[\text{Cl}^-]^2}\right) \\ &= 0.25\ \text{V} - [(0.0296\ \text{V})(8.37)] = 0.00\ \text{V} \end{aligned}$$

Thus the reaction will not occur spontaneously under these conditions (because E = 0 V and ΔG = 0). The composition specified is that of an equilibrium mixture

Exercise 20.6.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4\,\text{MnO}_2\,(s) + 3\,\text{O}_2\,(g) + 4\,\text{OH}^-\,(aq) \longrightarrow 4\,\text{MnO}_4^-\,(aq) + 2\,\text{H}_2\text{O}\,(l) \quad E^{\circ}_{cell} = -0.20\,V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, P_{O_2}= 0.20 atm, [MNO_4^-] = 1.0 × 10^{-4} M, and T = 25°C.

Answer available at the end of this section.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E°cell = 1.10V \tag{20.6.7}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0 × 10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 20.6.6:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \tag{20.6.8}$$

$$= 1.10\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right) \log \left(\frac{1.0 \times 10^{-6}}{1.0}\right) = 1.28\ \text{V} \tag{20.6.9}$$

Thus the initial voltage is greater than E° because $Q < 1$. As the reaction proceeds, [Zn^{2+}] in the anode compartment increases as the zinc electrode dissolves, while [Cu^{2+}] in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio Q = [Zn^{2+}]/[Cu^{2+}] steadily increases, and the cell voltage therefore steadily decreases. Eventually, [Zn^{2+}] = [Cu^{2+}], so Q = 1 and E_{cell} = E°$_{cell}$. Beyond this point, [Zn^{2+}] will continue to increase in the anode compartment, and [Cu^{2+}] will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0 × 10^{-6} M Cu^{2+}), Q = 1.0 × 10^{6}, and the cell potential will be reduced to 0.92 V.

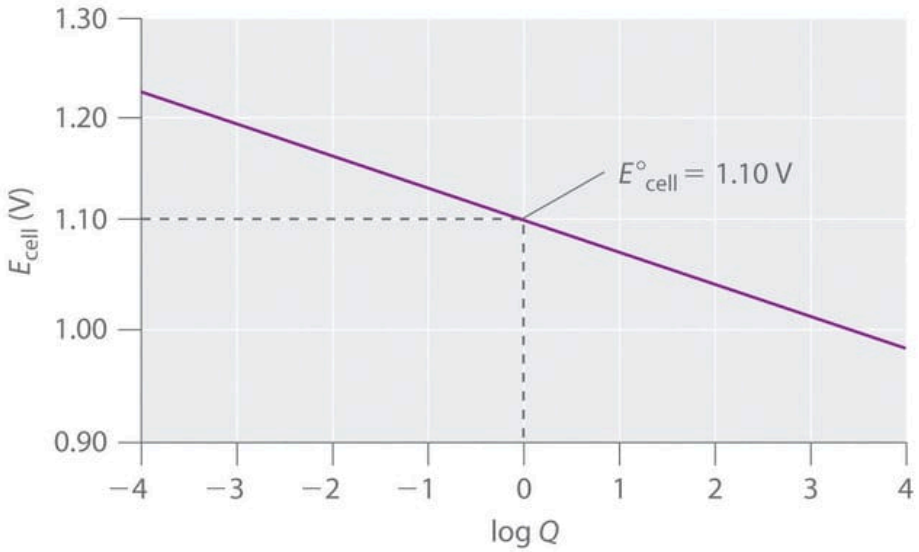


Figure 20.6.1: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than E°$_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When [Zn^{2+}] = [Cu^{2+}], log Q = 0 and E_{cell} = E°$_{cell}$ = 1.10 V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until Q = K and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

The variation of E_{cell} with $\log Q$ over this range is linear with a slope of −0.0591/n, as illustrated in Figure 20.6.1. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of Q when E_{cell} = 0 is calculated as follows:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q = 0 \tag{20.6.10}$$

$$E^{\circ} = \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{20.6.11}$$

$$\log Q = \frac{E^{\circ} n}{0.0591\ \text{V}} = \frac{(1.10\ \text{V})(2)}{0.0591\ \text{V}} = 37.23 \tag{20.6.12}$$

$$Q = 10^{37.23} = 1.7 \times 10^{37} \tag{20.6.13}$$

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+}

is 1.7 × 10^{37} at 25°C.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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The Nernst Equation: The Nernst Equation (opens in new window) [youtu.be]

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$\mathrm{Ag(s)\,|\,Ag^+}(aq, 0.010\ M)\,||\,\mathrm{Ag^+}(aq, 1.0\ M)\,|\,\mathrm{Ag\,(s)} \tag{20.6.14}$$

cathode:

$$\mathrm{Ag^+}(aq, 1.0\ M) + \mathrm{e^-} \rightarrow \mathrm{Ag\,(s)} \tag{20.6.15}$$

anode:

$$\mathrm{Ag\,(s)} \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) + \mathrm{e^-} \tag{20.6.16}$$

Overall

$$\mathrm{Ag^+}(aq, 1.0\ M) \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) \tag{20.6.17}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0 - \left(\frac{0.0591\ \text{V}}{1}\right)\log\left(\frac{0.010}{1.0}\right) \\ &= 0.12\ \text{V} \end{aligned}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero (E_{cell} = 0).

Example 20.6.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2 × 10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.
B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$[redacted](aq, 2.0\,M) \rightarrow [redacted](aq, 5.2 \times 10^{-2}\,M)$$

B For the reduction of Mn^{2+}(aq) to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 20.6.6:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{5.2 \times 10^{-2}}{2.0}\right) \\ &= 0.047\ \text{V} \end{aligned}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

Exercise 20.6.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$\mathrm{O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \rightarrow 2\,H_2O\,(l)}$$

What will be the potential when the circuit is closed?

Answer available at the end of this section.

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned previously, solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

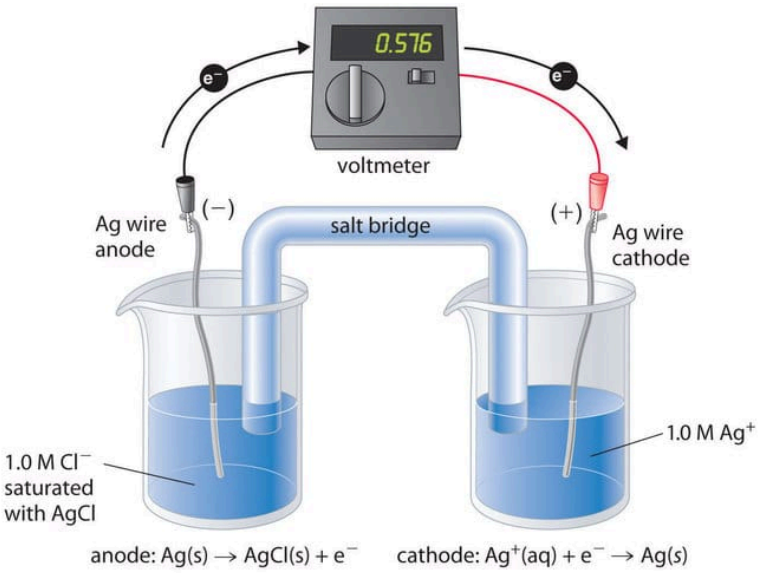


Figure 20.6.1: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in [Ag^+] between the two cells can be used to determine K_{sp}. (CC BY-NC-SA; Anonymous by request)

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 20.6.1, which is designed to measure the solubility product of silver chloride:

$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}].$$

In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by [Cl^-] and substituting:

$$\begin{aligned}[\mathrm{Ag^+}] &= \frac{K_{sp}}{[\mathrm{Cl^-}]} \\ &= \frac{K_{sp}}{1.0} = K_{sp}.\end{aligned}$$

The overall cell reaction is as follows:

$$\mathrm{Ag^+(aq,\ concentrated)} \rightarrow \mathrm{Ag^+(aq,\ dilute)}$$

Thus the voltage of the concentration cell due to the difference in [Ag^+] between the two cells is as follows:

$$\begin{aligned}E_{\text{cell}} &= 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{1}\right)\log\left(\frac{[\mathrm{Ag^+}]_{\text{dilute}}}{[\mathrm{Ag^+}]_{\text{concentrated}}}\right) \\ &= -0.0591\ \text{V}\ \log\left(\frac{K_{\text{sp}}}{1.0}\right) \\ &= -0.0591\ \text{V}\ \log K_{\text{sp}}\end{aligned} \tag{20.6.18}$$

By closing the circuit, we can measure the potential caused by the difference in [Ag+] in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 20.6.18 for K_{sp},

$$\log K_{\text{sp}} = \frac{-E_{\text{cell}}}{0.0591\ \text{V}} = \frac{-0.580\ \text{V}}{0.0591\ \text{V}} = -9.81$$

$$K_{\text{sp}} = 1.5 \times 10^{-10}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a

sparingly soluble salt.

Example 20.6.3: Solubility of lead(II) sulfate

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure 20.6.1, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A. From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.
B. Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation ??? and solve for K_{sp}.

Solution

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of Pb^{2+} and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$[Pb^{2+}][SO_4^{2-}] = K_{sp}$$
$$[Pb^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{K_{sp}}{1.0\ M} = K_{sp}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

$$Pb^{2+}(aq, concentrated) \rightarrow Pb^{2+}(aq, dilute)$$

so

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591}{n}\right) \log Q$$
$$0.230\ V = 0\ V - \left(\frac{0.0591\ V}{2}\right) \log \left(\frac{[Pb^{2+}]_{dilute}}{[Pb^{2+}]_{concentrated}}\right) = -0.0296\ V \log\left(\frac{K_{sp}}{1.0}\right)$$
$$-7.77 = \log K_{sp}$$
$$1.7 \times 10^{-8} = K_{sp}$$

Exercise 20.6.3

A concentration cell similar to the one described in Example 20.6.3 contains a 1.0 M solution of lanthanum nitrate [$La(NO_3)_3$] in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer available at the end of this section.

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example 20.6.3, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated below.

Example 20.6.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment. The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$$\mathrm{Zn\,(s)|Zn^{2+}}(aq, 1.0\,M)||\mathrm{H^+}(aq, ?\,M)|\mathrm{H_2}(g, 1.0\,atm)|Pt(s)$$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A. Write the overall cell reaction.
B. Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table P2):

$$Zn(s) + 2H^{2+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \quad E°=0.76\ V$$

B By substituting the given values into the simplified Nernst equation (Equation 20.6.6), we can calculate $[H^+]$ under nonstandard conditions:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log\left(\frac{[\mathrm{Zn^{2+}}]P_{\mathrm{H_2}}}{[\mathrm{H^+}]^2}\right)$$

$$0.26\ \text{V} = 0.76\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{(1.0)(1.0)}{[\mathrm{H^+}]^2}\right)$$

$$16.9 = \log\left(\frac{1}{[\mathrm{H^+}]^2}\right) = \log\,[\mathrm{H^+}]^{-2} = (-2)\log[\mathrm{H^+}]$$

$$8.46 = -\log[\mathrm{H^+}]$$

$$8.5 = \mathrm{pH}$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise 20.6.4

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows:

$$Pb_{(s)} \mid Pb^{2+}(aq, ?M) \parallel H^{+}(aq), 1.0M \mid O_2(g, 1.0atm) \mid Pt_{(s)}$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table P2 to determine the concentration of Pb^{2+} in the groundwater.

Answer available at the end of this section.

Summary

The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution. The Nernst equation allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. Concentration cells consist of anode and cathode compartments that are identical except for the concentrations of the reactant. Because $\Delta G = 0$ at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

Answers

Exercise 20.6.1

E_{cell} = −0.22 V; the reaction will not occur spontaneously.

Exercise 20.6.2

0.41 V

Exercise 20.6.3

5.7×10^{-17}

Exercise 20.6.4

$1.2 \times 10^{-9}\ M$

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20.7: Batteries and Fuel Cells

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure 20.7.1). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (–) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

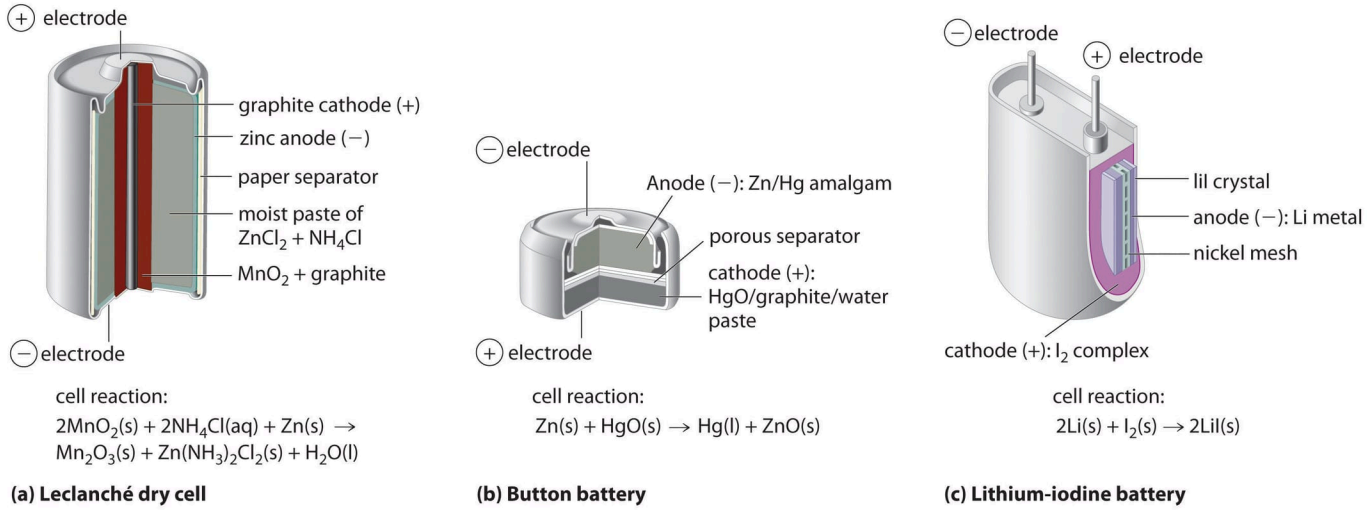


Figure 20.7.1: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a “wet cell”: the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure $20.7.1$). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2\,\mathrm{MnO_2\,(s)} + 2\,\mathrm{NH_4^+\,(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3\,(s)} + 2\,\mathrm{NH_3\,(aq)} + \mathrm{H_2O\,(l)}$$

- anode (oxidation):

$$\mathrm{Zn\,(s)} \longrightarrow \mathrm{Zn^{2+}\,(aq)} + 2\,\mathrm{e^-}$$

The $\mathrm{Zn^{2+}}$ ions formed by the oxidation of $\mathrm{Zn\,(s)}$ at the anode react with $\mathrm{NH_3}$ formed at the cathode and $\mathrm{Cl^-}$ ions present in solution, so the overall cell reaction is as follows:

- overall reaction:

$$2\,\mathrm{MnO_2\,(s)} + 2\,\mathrm{NH_4Cl\,(aq)} + \mathrm{Zn\,(s)} \longrightarrow \mathrm{Mn_2O_3\,(s)} + \mathrm{Zn(NH_3)_2Cl_2\,(s)} + \mathrm{H_2O\,(l)} \tag{20.7.1}$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the $\mathrm{MnO_2}$ that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with $\mathrm{NH_4Cl}$ in the electrolyte, causing the case to corrode and allowing the contents to leak out.

Close up of a hand holding one double <span class=
AA
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Source: Photo courtesy of Mitchclanky2008, www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$2\,\mathrm{MnO_2\,(s)} + \mathrm{H_2O\,(l)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3\,(s)} + 2\,\mathrm{OH^-\,(aq)}$$

- anode (oxidation):

$$\mathrm{Zn\,(s)} + 2\,\mathrm{OH^-\,(aq)} \longrightarrow \mathrm{ZnO\,(s)} + \mathrm{H_2O\,(l)} + 2\,\mathrm{e^-}$$

- overall reaction:

$$\mathrm{Zn\,(s)} + 2\,\mathrm{MnO_2\,(s)} \longrightarrow \mathrm{ZnO\,(s)} + \mathrm{Mn_2O_3\,(s)}$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or $\mathrm{Ag_2O}$ as the oxidant rather than $\mathrm{MnO_2}$ in Figure $20.7.1b$).



Button batteries. (Gerhard H Wrodnigg via Wikipedia)

The cathode, anode and overall reactions and cell output for these two types of button batteries are as follows (two half-reactions occur at the anode, but the overall oxidation half-reaction is shown):

- cathode (mercury battery):

$$\mathrm{HgO\,(s) + H_2O\,(l) + 2\,e^- \longrightarrow Hg\,(l) + 2\,OH^-\,(aq)}$$

- Anode (mercury battery):

$$\mathrm{Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-}$$

- overall reaction (mercury battery):

$$\mathrm{Zn\,(s) + 2\,HgO\,(s) \longrightarrow 2\,Hg\,(l) + ZnO\,(s)}$$

  with $E_{cell} = 1.35\ V$.
- cathode reaction (silver battery):

$$\mathrm{Ag_2O\,(s) + H_2O\,(l) + 2\,e^- \longrightarrow 2\,Ag\,(s) + 2\,OH^-\,(aq)}$$

- anode (silver battery):

$$\mathrm{Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-}$$

- Overall reaction (silver battery):

$$\mathrm{Zn\,(s) + 2\,Ag_2O\,(s) \longrightarrow 2\,Ag\,(s) + ZnO\,(s)}$$

  with $E_{cell} = 1.6\ V$.

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually “dry.” They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-{}_{(LiI)} \tag{20.7.2}$$

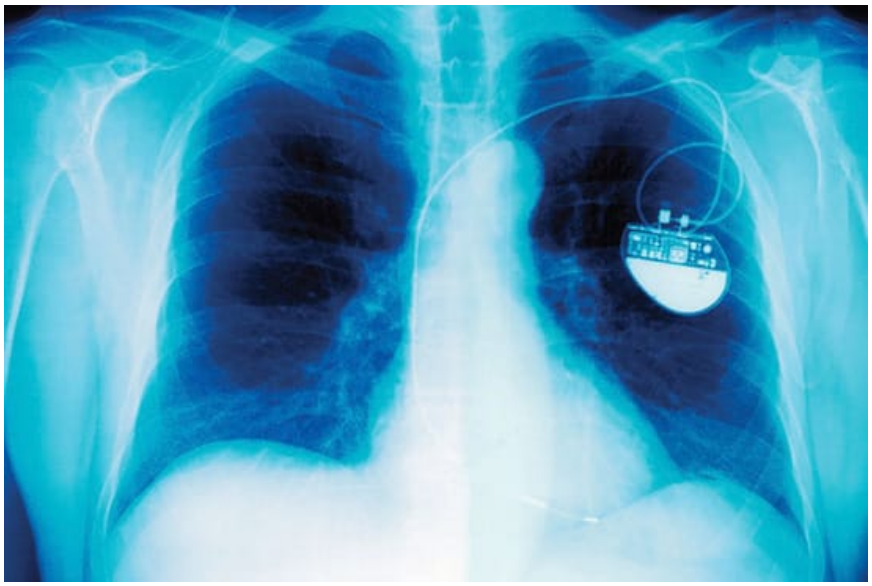
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{20.7.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{20.7.4}$$

with $E_{cell} = 3.5\ V$



Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure $20.7.1$, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure $20.7.2$, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

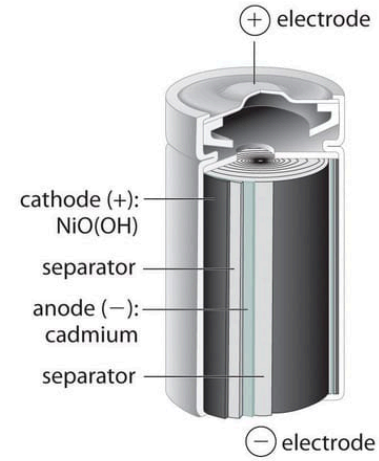


Figure 20.7.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a $NiCad$ battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{20.7.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{20.7.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{20.7.7}$$

$$E_{cell} = 1.4V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

\[NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \label{Eq16} \]

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

> Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells.

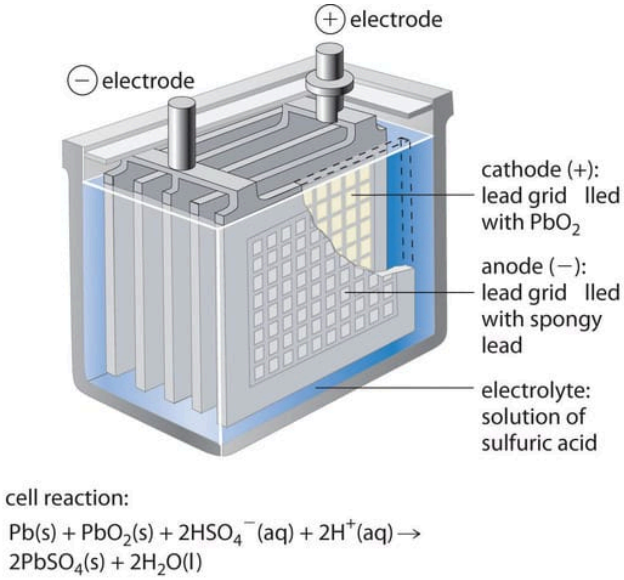


Figure 20.7.3: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As shown in Figure 20.7.3, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):

\[PbO_{2(s)} + HSO^–_{4(aq)} + 3H^+_{(aq)} + 2e^– \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \label{Eq17} \]

with $E^\circ_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{20.7.8}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{20.7.9}$$

and $E^\circ_{cell} = 2.041\ V$

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{20.7.10}$$

This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

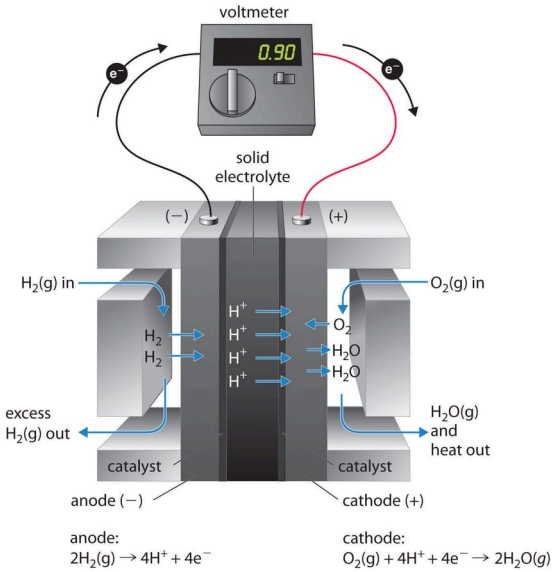


Figure 20.7.4: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of $H_2(g)$ and $O_2(g)$, as illustrated in Figure 20.7.4. The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{20.7.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{20.7.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{20.7.13}$$

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

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20.8: Corrosion

Learning Objectives

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

Corrosion is a REDOX process.

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($\mathrm{Fe_2O_3 \cdot \mathit{x}\,H_2O}$), commonly known as rust, that does not provide a tight protective film (Figure $20.8.1$). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil will not rust because of the absence of water even if the solvent is saturated with oxygen.

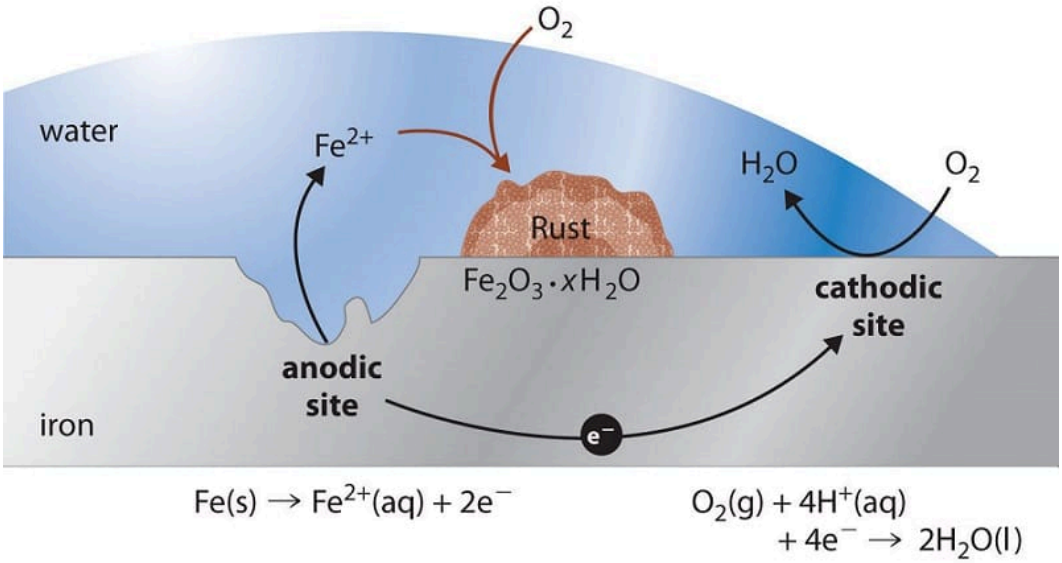


Figure $20.8.1$: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to $Fe^{2+}(aq)$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3 \bullet xH_2O$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen. (CC BY-NC-SA; anonymous)

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$\mathrm{O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \longrightarrow 2\,H_2O\,(l)}$$

  with $E^o_{SRP} = 1.23\ V$.
- at anode:

$$\mathrm{Fe\,(s) \longrightarrow Fe^{2+}\,(aq) + 2\,e^-}$$

  with $E^o_{SRP} = -0.45\ V$.
- overall:

$$\mathrm{2\,Fe\,(s) + O_2\,(g) + 4\,H^+\,(aq) \longrightarrow 2\,Fe^{2+}\,(aq) + 2\,H_2O\,(l)} \tag{20.8.1}$$

  with $E^o_{cell} = 1.68\ V$.

The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+}, as represented in the following equation:

$$\mathrm{4\,Fe^{2+}\,(aq) + O_2\,(g) + (2 + 4\,x)H_2O \ \rightarrow 2\,Fe_2O_3 \ \cdot x\,H_2O + 4\,H^+\,(aq)} \tag{20.8.2}$$

The sign and magnitude of E^o_{cell} for the corrosion process (Equation 20.8.1) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 20.8.2).

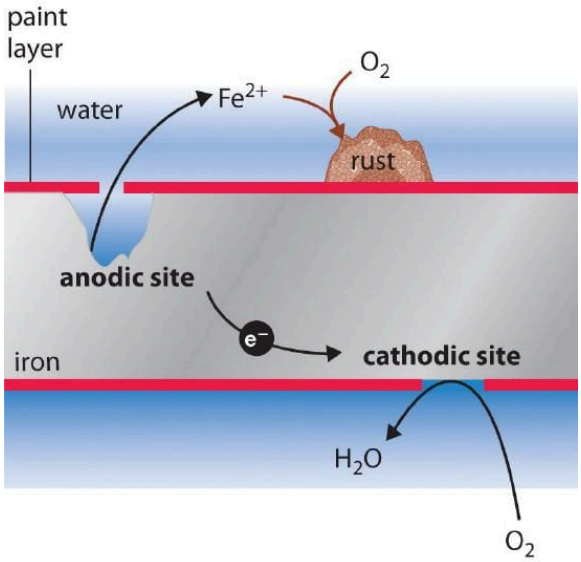


Figure 20.8.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually consist of steel container that is coated with a thin layer of tin. While neither chromium nor tin metals are intrinsically resistant to corrosion, they both form protective oxide coatings that hinder access of oxygen and water to the underlying steel (iron alloy).

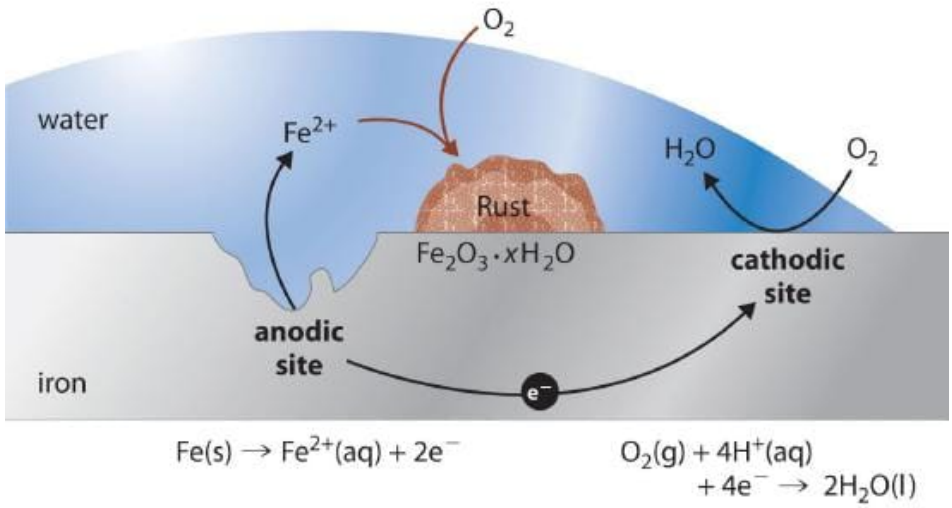


Figure 20.8.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for $\mathrm{Sn^{2+}}$ (E° = −0.14 V) and $\mathrm{Fe^{2+}}$ (E° = −0.45 V) in Table P2 show that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 20.8.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as Zn (E° = −0.76 V for $\mathrm{Zn^{2+} + 2\,e^- \longrightarrow Zn}$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{20.8.3}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{20.8.4}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{20.8.5}$$

The more reactive metal reacts with oxygen and will eventually dissolve, "sacrificing" itself to protect the iron object. Cathodic

protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.



Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 20.8.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

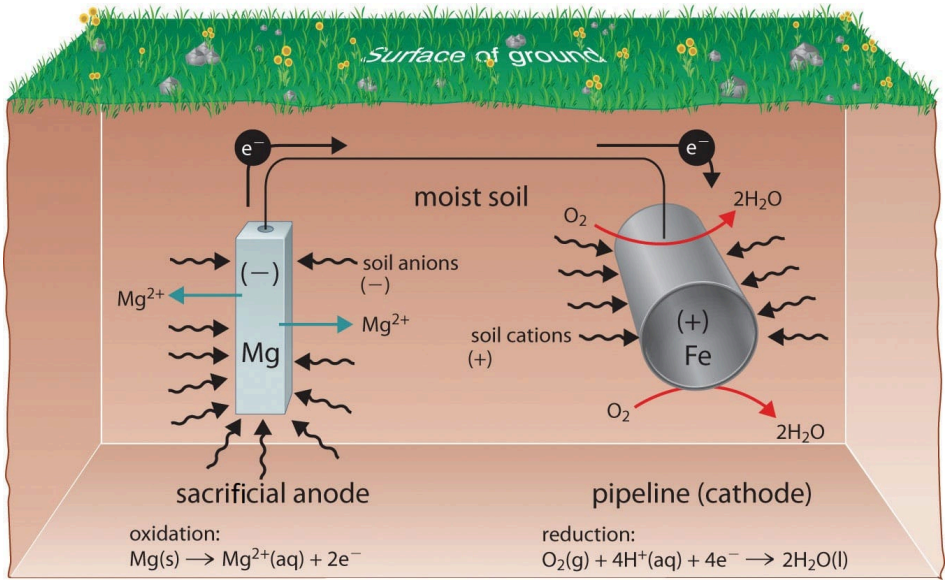


Figure 20.8.4: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium ($E° = -2.37$ V) is much more easily oxidized than iron ($E° = -0.45$ V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

Example 20.8.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E^{o}{}^{\circ}{}_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E^o\,^\circ{}_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E^o\,^\circ{}_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E^o\,^\circ{}_{cell}$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

$$\begin{array}{lll} \text{cathode:} & \mathrm{O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)} & E^\circ_{\text{cathode}} = 1.23\ \text{V} \\ \text{anode:} & \mathrm{Fe(s) \rightarrow Fe^{2+} + 2e^-} & E^\circ_{\text{anode}} = -0.45\ \text{V} \\ \text{overall:} & \mathrm{2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)} & E^\circ_{\text{overall}} = 1.68\ \text{V} \end{array}$$

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 20.8.5).



Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

Exercise 20.8.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a available at the end of this section.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

Answers

Exercise $20.8.1$

Not unless you plan to sell the house very soon because the $\mathrm{Cu/Fe}$ pipe joints will lead to rapid corrosion.

Any existing $\mathrm{Pb/Fe}$ joints should be examined carefully for corrosion of the iron pipes due to the $\mathrm{Pb-Fe}$ junction; the less active Pb will have served as the cathode for the reduction of $\mathrm{O_2}$, promoting oxidation of the more active Fe nearby.

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20.9: Electrolysis

Learning Objectives

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a $1\ M\ Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure $20.9.1a$).

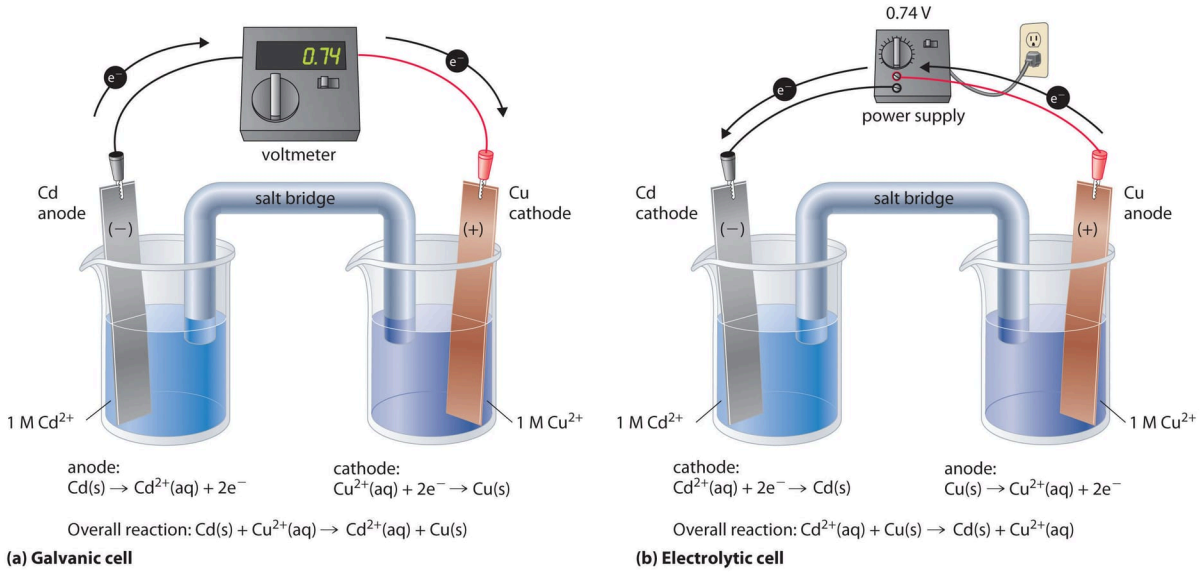


Figure $20.9.1$: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it. (CC BY-SA-NC; anonymous)

The overall reaction is as follows:

$$\mathrm{Cd\,(s) + Cu^{2+}\,(aq)\ \rightarrow Cd^{2+}\,(aq) + Cu\,(s)}$$

with $E\,^{\circ}{}_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G^{o} < 0$):

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ &= -(2\text{ mol e}^-)[96,485\text{ J/(V}\cdot\text{mol)}](0.74\text{ V}) \\ &= -140\text{ kJ (per mole Cd)}\end{aligned}$$

In this direction, the system is acting as a galvanic cell.

In an electrolytic cell, an external voltage is applied to drive a *nonspontaneous* reaction.

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure $20.9.1b$). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- half-reaction at the cathode:

$$\text{Cd}^{2+}\,(\text{aq}) + 2\,\text{e}^- \rightarrow \text{Cd}\,(\text{s}) \tag{20.9.1}$$

with $E^\circ_{cathode} = -0.40\ V$

- half-reaction at the anode:

$$\text{Cu}\,(\text{s}) \rightarrow \text{Cu}^{2+}\,(\text{aq}) + 2\,\text{e}^- \tag{20.9.2}$$

with $E^\circ_{anode} = 0.34\ V$

- Overall Reaction:

$$\text{Cd}^{2+}\,(\text{aq}) + \text{Cu}\,(\text{s}) \rightarrow \text{Cd}\,(\text{s}) + \text{Cu}^{2+}\,(\text{aq}) \tag{20.9.3}$$

with $E^\circ_{cell} = -0.74\ V$

Because $E^\circ_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table $20.9.1$.

Table $20.9.1$: Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	–	+
cathode	+	–

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten NaCl, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

$$2\,\mathrm{NaCl}\,(\mathrm{l}) \;\rightarrow 2\,\mathrm{Na}\,(\mathrm{l}) + \mathrm{Cl_2}\,(\mathrm{g}) \tag{20.9.4}$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C, well below that of NaCl (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten NaCl in a Downs cell (Figure 20.9.2). In this specialized cell, $\mathrm{CaCl_2}$ (melting point = 772°C) is first added to the NaCl to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

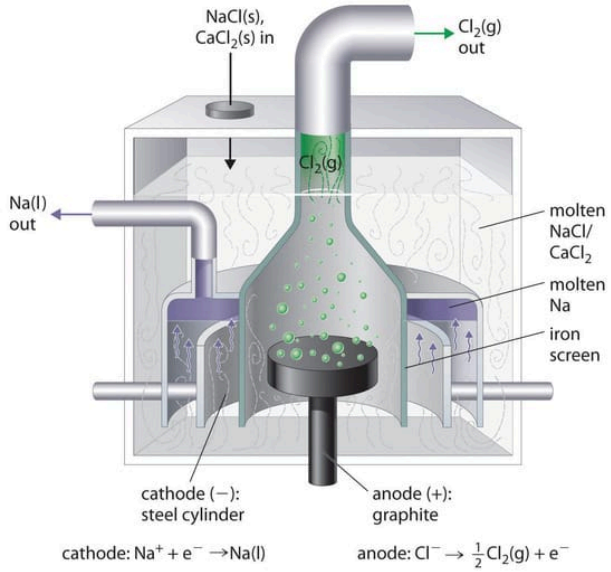


Figure 20.9.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact. (CC BY-SA-NC; anonymous)

Similarly, in the Hall–Heroult process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2\,\mathrm{Al_2O_3}\,(\mathrm{l}) + 3\,\mathrm{C}\,(\mathrm{s}) \longrightarrow 4\,\mathrm{Al}\,(\mathrm{l}) + 3\,\mathrm{CO_2}\,(\mathrm{g}) \tag{20.9.5}$$

Oxide ions react with oxidized carbon at the anode, producing CO_2(g).

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of

complex ions, become important and may determine the outcome.

Example 20.9.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A. List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5, determine which species will be reduced and which species will be oxidized.
B. Identify the products that will form at each electrode.

Solution

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

Exercise 20.9.1

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer available at the end of this section.

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 20.9.3).

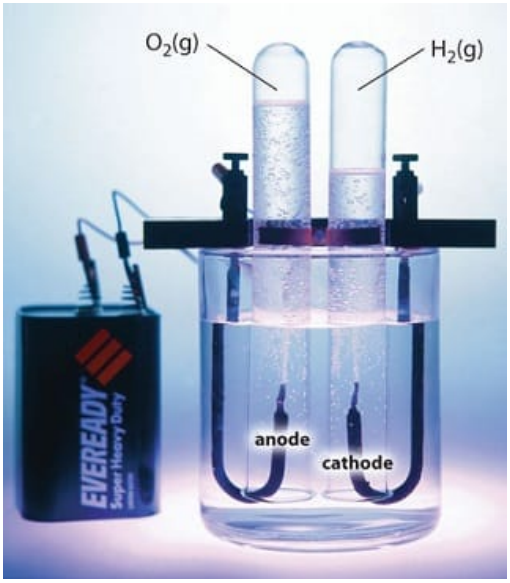


Figure 20.9.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{20.9.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{20.9.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{20.9.8}$$

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2} = 1$ atm, we can use the standard potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log(P_{O_2}P^2_{H_2}) \tag{20.9.9}$$

$$= -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right)\log(1) = -1.23\ \text{V} \tag{20.9.10}$$

Thus E_{cell} is –1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 20.9.4.

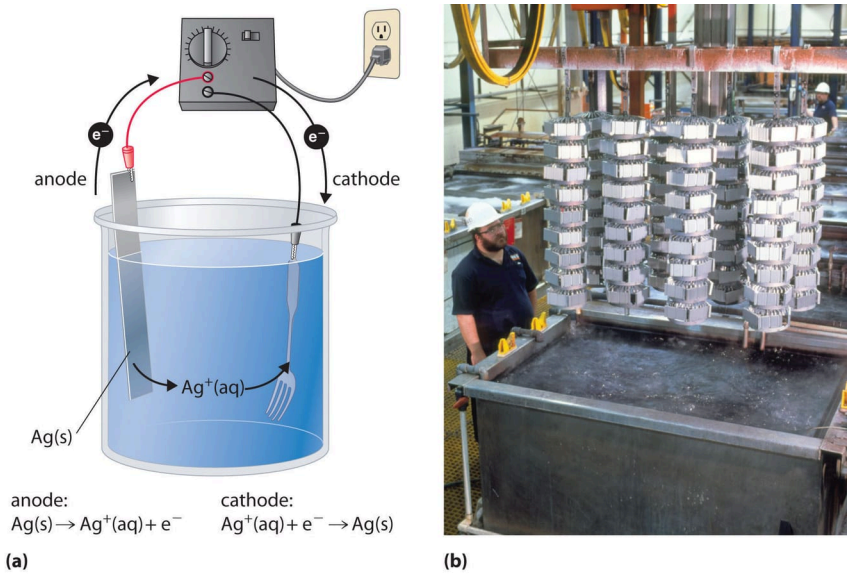


Figure 20.9.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag^+ solution and applying the correct potential. (CC BY-SA-NC; anonymous)

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E°_{cathode} = 0.80V$$

- anode (silver bar):

$$Ag(s) \longrightarrow Ag^+(aq) + e^- \qquad E°_{anode} = 0.80V$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E^o_{cell} = 0\ V$, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the

stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)}$$

1 mol of electrons reduces 1 mol of $\mathrm{Ag^+}$ to Ag metal. In contrast, in the reaction

$$\mathrm{Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)}$$

1 mol of electrons reduces only 0.5 mol of $\mathrm{Cu^{2+}}$ to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,485 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (q in coulombs) transferred is the product of the current (I in amperes) and the time (t, in seconds):

$$q = I \times t \tag{20.9.11}$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $\mathrm{CuSO_4}$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\begin{aligned} q &= (0.60\ \mathrm{A})(6.0\ \mathrm{min})(60\ \mathrm{s/min}) \\ &= 220\ \mathrm{A \cdot s} \\ &= 220\ \mathrm{C} \end{aligned}$$

The number of moles of electrons transferred to $\mathrm{Cu^{2+}}$ is therefore

$$\begin{aligned} \mathrm{moles\ e^-} &= \frac{220\ \mathrm{C}}{96{,}485\ \mathrm{C/mol}} \\ &= 2.3 \times 10^{-3}\ \mathrm{mol\ e^-} \end{aligned}$$

Because two electrons are required to reduce a single $\mathrm{Cu^{2+}}$ ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

Example 20.9.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A. Calculate the number of moles of metal corresponding to the given mass transferred.
B. Write the reaction and determine the number of moles of electrons required for the electroplating process.
C. Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$\text{moles Ag} = \frac{2.00\ \text{g}}{107.868\ \text{g/mol}} = 1.85 \times 10^{-2}\ \text{mol Ag}$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$\text{coulombs} = (1.85 \times 10^{-2}\text{mol } e^-)(96{,}485\ \text{C/mol } e^-) = 1.78 \times 10^3\ \text{C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\begin{aligned}\text{amperes} &= \frac{1.78 \times 10^3\ \text{C}}{(12.0\ \text{h})(60\ \text{min/h})(60\ \text{s/min})} \\ &= 4.12 \times 10^{-2}\ \text{C/s} = 4.12 \times 10^{-2}\ \text{A}\end{aligned}$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

Exercise 20.9.2

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Electroplating: Electroplating(opens in new window) [youtu.be]

Summary

In electrolysis, an external voltage is applied to drive a **nonspontaneous** reaction. The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred. Relationship of charge, current and time:

$$q = I \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an overvoltage, must be applied to overcome factors such as a large activation energy and a junction potential. Electroplating is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

Answers

Exercise 20.9.1

Br_2 and Al

Exercise 20.9.2

5.8 h

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20.E: Electrochemistry (Exercises)

Questions moved to ADAPT.

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21: NUCLEAR CHEMISTRY

Until now, you have studied chemical processes in which atoms share or transfer electrons to form new compounds, leaving the atomic nuclei largely unaffected. In this chapter, we examine some properties of the atomic nucleus and the changes that can occur in atomic nuclei. Nuclear reactions differ from other chemical processes in one critical way: in a nuclear reaction, **the identities of the elements change**. In addition, nuclear reactions are often accompanied by the release of enormous amounts of energy, as much as a *billion* times more than the energy released by chemical reactions. Moreover, the yields and rates of a nuclear reaction are generally unaffected by changes in temperature, pressure, or the presence of a catalyst.

We begin by examining the structure of the atomic nucleus and the factors that determine whether a particular nucleus is stable or decays spontaneously to another element. We then discuss the major kinds of nuclear decay reactions, as well as the properties and uses of the radiation emitted when nuclei decay. You will learn how radioactive emissions can be used to study the mechanisms of chemical reactions and biological processes and how to calculate the amount of energy released during a nuclear reaction. You will also discover why houses are tested for radon gas, how radiation is used to probe organs such as the brain, and how the energy from nuclear reactions can be harnessed to produce electricity. Last, we explore the nuclear chemistry that takes place in stars, and we describe the role that stars play in producing most of the elements in the universe.

21.1: Radioactivity

21.2: Patterns of Nuclear Stability

21.3: Nuclear Transmutations

21.4: Rates of Radioactive Decay

21.5: Energy Changes in Nuclear Reactions

21.6: Nuclear Fission

21.7: Nuclear Fusion

21.8: Biological Effects of Radiation

21.E: Exercises

21.S: Nuclear Chemistry (Summary)

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21.1: Radioactivity

Learning Objectives

- Write and balance nuclear equations
- To know the different kinds of radioactive decay.
- To balance a nuclear reaction.

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of $^{1}_{1}\mathrm{H}$, neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term nuclide and identify it by the notation:

$$^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X} \tag{21.1.1}$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, $^{14}_{6}\mathrm{C}$ is called "carbon-14."

Protons and neutrons, collectively called nucleons, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^{6} meters, 30,000 times larger).

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Nuclear Equations

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_{8}\mathrm{O}$ is a product of the nuclear reaction of $^{14}_{7}\mathrm{N}$ and $^{4}_{2}\mathrm{He}$ if we knew that a proton, $^{1}_{1}\mathrm{H}$, was one of the two products. Example $21.1.1$ shows how we can identify a nuclide by balancing the

nuclear reaction.

Example 21.1.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 ($^{25}_{12}\mathrm{Mg}$) produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$^{25}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X}$$

where

- A is the mass number and
- Z is the atomic number of the new nuclide, X.

Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = \mathrm{A} + 1$$

so

$$\mathrm{A} = 28$$

Similarly, the charges must balance, so:

$$12 + 2 = \mathrm{Z} + 1$$

so

$$\mathrm{Z} = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is $^{28}_{13}\mathrm{Al}$.

Exercise 21.1.1

The nuclide $^{125}_{53}\mathrm{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer available at the end of this section.

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions**.** In a **nuclear decay reaction**, also called radioactive decay, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting daughter nuclei have a lower mass and are lower in energy (more stable) than the parent nucleus that decayed. In contrast, in a **nuclear transmutation reaction**, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

> Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.

Nuclear Decay Reactions

Just as we use the number and type of atoms present to balance a chemical equation, we can use the number and type of nucleons present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, the total number of nucleons is conserved in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the ${}^{A}_{Z}\mathrm{X}$ notation for nuclides to include radioactive emissions. Table 21.1.1 lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

Table 21.1.1: Nuclear Decay Emissions and Their Symbols

Identity	Symbol	Charge	Mass (amu)
helium nucleus	${}^{4}_{2}\alpha$	+2	4.001506
electron	${}^{0}_{-1}\beta$ or β^{-}	–1	0.000549
photon	${}^{0}_{0}\gamma$	—	—
neutron	${}^{1}_{0}\mathrm{n}$	0	1.008665
proton	${}^{1}_{1}\mathrm{p}$	+1	1.007276
positron	${}^{0}_{+1}\beta$ or β^{+}	+1	0.000549

Like the notation used to indicate isotopes, the upper left superscript in the symbol for a particle gives the mass number, which is the total number of protons and neutrons. For a proton or a neutron, $A = 1$. Because neither an electron nor a positron contains protons or neutrons, its mass number is 0. The numbers should not be taken literally, however, as meaning that these particles have zero mass; ejection of a beta particle (an electron) simply has a negligible effect on the mass of a nucleus.

Similarly, the lower left subscript gives the charge of the particle. Because protons carry a positive charge, $Z = +1$ for a proton. In contrast, a neutron contains no protons and is electrically neutral, so $Z = 0$. In the case of an electron, $Z = –1$, and for a positron, $Z = +1$. Because γ rays are high-energy photons, both A and Z are 0. In some cases, two different symbols are used for particles that are identical but produced in different ways. For example, the symbol ${}^{0}_{-1}\mathrm{e}$, which is usually simplified to e^{-}, represents a free electron or an electron associated with an atom, whereas the symbol ${}^{0}_{-1}\beta$, which is often simplified to β^{-}, denotes an electron that originates from within the nucleus, which is a β particle. Similarly, ${}^{4}_{2}\mathrm{He}^{2+}$ refers to the nucleus of a helium atom, and ${}^{4}_{2}\alpha$ denotes an identical particle that has been ejected from a heavier nucleus.

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure 21.1.1. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.

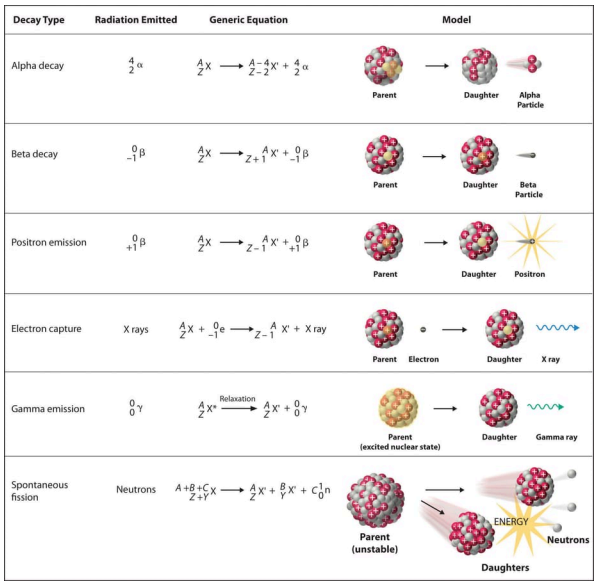


Figure 21.1.1: Common Modes of Nuclear Decay

The different types of decay are alpha, beta, positron emission, electron capture, gamma emission, and spontaneous fission.

Alpha α Decay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, ${}^{4}_{2}\alpha$. The general reaction is as follows:

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A-4}_{Z-2}\text{X}'} + \underset{\substack{\text{alpha}\\\text{particle}}}{{}^{4}_{2}\alpha} \tag{21.1.2}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha \tag{21.1.3}$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

> Just as the total number of atoms is conserved in a chemical reaction, the total number of nucleons is conserved in a nuclear reaction.

Beta β^- Decay

Nuclei that contain too many neutrons often undergo **beta (β) decay**, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^{0}_{-1}\beta} \tag{21.1.4}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{21.1.5}$$

Although beta decay does not change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$$^{14}_{6}\mathrm{C} \rightarrow ^{14}_{7}\mathrm{N} + ^{0}_{-1}\beta$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

Positron β^+ Emission

Because a positron has the same mass as an electron but opposite charge, **positron emission** is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

$$^{1}_{1}\mathrm{p}^{+} \rightarrow ^{1}_{0}\mathrm{n} + ^{0}_{+1}\beta^{+} \tag{21.1.6}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{^{A}_{Z}\mathrm{X}} \rightarrow \underset{\text{daughter}}{^{A}_{Z-1}\mathrm{X}'} + \underset{\text{positron}}{^{0}_{+1}\beta^{+}}$$

Like beta decay, positron emission does not change the mass number of the nucleus. In this case, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Thus the neutron-to-proton ratio has increased, again moving the nucleus closer to the band of stable nuclei. For example, carbon-11 undergoes positron emission to form boron-11:

$$^{11}_{6}\mathrm{C} \rightarrow ^{11}_{5}\mathrm{B} + ^{0}_{+1}\beta^{+}$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

Electron Capture

A neutron-poor nucleus can decay by either positron emission or **electron capture (EC)**, in which an electron in an inner shell reacts with a proton to produce a neutron:

$$^{1}_{1}\mathrm{p} + ^{0}_{-1}\mathrm{e} \rightarrow ^{1}_{0}\mathrm{n} \tag{21.1.7}$$

When a second electron moves from an outer shell to take the place of the lower-energy electron that was absorbed by the nucleus, an x-ray is emitted. The overall reaction for electron capture is thus

$$\underset{\text{parent}}{^{A}_{Z}\mathrm{X}} + \underset{\text{electron}}{^{0}_{-1}\mathrm{e}} \rightarrow \underset{\text{daughter}}{^{A}_{Z-1}\mathrm{X}'} + \text{x-ray}$$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

$$^{55}_{26}\mathrm{Fe} \overset{\mathrm{EC}}{\rightarrow} ^{55}_{25}\mathrm{Mn} + \text{x-ray}$$

The atomic numbers of the parent and daughter nuclides differ in Equation 20.2.11, although the mass numbers are the same. To write a balanced nuclear equation for this reaction, we must explicitly include the captured electron in the equation:

$$^{55}_{26}\mathrm{Fe} + ^{0}_{-1}\mathrm{e} \rightarrow ^{55}_{25}\mathrm{Mn} + \text{x-ray}$$

Both positron emission and electron capture are usually observed for nuclides with low neutron-to-proton ratios, but the decay rates for the two processes can be very different.

Gamma γ Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. These high-energy photons are γ rays. **Gamma** (γ) **emission** can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$^{238}_{92}\mathrm{U} \rightarrow \underset{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}}{^{234}_{90}\mathrm{Th}^{*}} + ^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\mathrm{Th} + {}^{0}_{0}\gamma$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\mathrm{Th}^{*} \rightarrow {}^{234}_{88}\mathrm{Th} + {}^{0}_{0}\gamma$$

or more generally,

$$^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Spontaneous Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of $^{254}_{98}\mathrm{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$^{254}_{98}\mathrm{Cf} \rightarrow {}^{118}_{46}\mathrm{Pd} + {}^{132}_{52}\mathrm{Te} + 4{}^{1}_{0}\mathrm{n}$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

Example 21.1.2

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\mathrm{S}$
b. the decay of $^{201}_{80}\mathrm{Hg}$ by electron capture
c. the decay of $^{30}_{15}\mathrm{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as ${}^{A}_{Z}\mathrm{X}$:

$$ {}^{35}_{16}\mathrm{S} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta $$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of *A* = 35 − 0 = 35 and an atomic number of *Z* = 16 − (−1) = 17. The element with *Z* = 17 is chlorine, so the balanced nuclear equation is as follows:

$$ {}^{35}_{16}\mathrm{S} \rightarrow {}^{35}_{17}\mathrm{Cl} + {}^{0}_{-1}\beta $$

b.

A We know the identities of both reactants: ${}^{201}_{80}\mathrm{Hg}$ and an inner electron, ${}^{0}_{-1}\mathrm{e}$. The reaction is as follows:

$$ {}^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z}\mathrm{X} $$

B Both protons and neutrons are conserved, so the mass number of the product must be *A* = 201 + 0 = 201, and the atomic number of the product must be *Z* = 80 + (−1) = 79, which corresponds to the element gold. The balanced nuclear equation is thus

$$ {}^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{201}_{79}\mathrm{Au} $$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$ {}^{30}_{15}\mathrm{P} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{+1}\beta $$

B The mass number of the second product is *A* = 30 − 0 = 30, and its atomic number is *Z* = 15 − 1 = 14, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$ {}^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}\beta $$

Exercise 21.1.2

Write a balanced nuclear equation to describe each reaction.

a. ${}^{11}_{6}\mathrm{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from ${}^{185}_{74}\mathrm{W}$

Answer a available at the end of this section.

Example 21.1.3

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. ${}^{45}_{22}\mathrm{Ti}$
b. ${}^{242}_{94}\mathrm{Pu}$
c. ${}^{12}_{5}\mathrm{B}$
d. ${}^{256}_{100}\mathrm{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of *Z*, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{242}_{94}\mathrm{Pu}$ is expected to decay by alpha emission.
c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}\mathrm{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}\mathrm{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

Exercise 21.1.3

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{32}_{14}\mathrm{Si}$
b. $^{43}_{21}\mathrm{Sc}$
c. $^{231}_{91}\mathrm{Pa}$

Answer a available at the end of this section.

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases *Z* by only 2, and positron emission or electron capture decreases *Z* by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and beta-decay reactions is called a **radioactive decay series**. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure 21.1.2). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of “only” 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

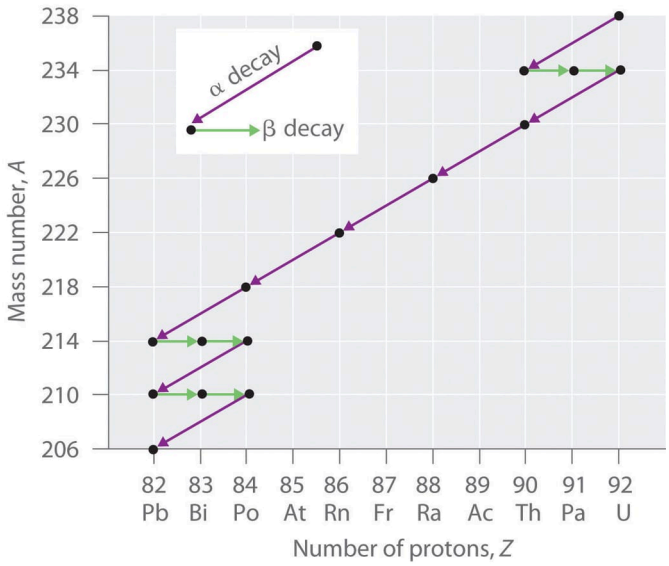


Figure 21.1.2 A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

Graph of mass number against number of protons. The purple lines are alpha decay which are linear while the green lines are beta decay and are horizontal and parallel to the x axis.

Due to these radioactive decay series, small amounts of very unstable isotopes are found in ores that contain uranium or thorium. These rare, unstable isotopes should have decayed long ago to stable nuclei with a lower atomic number, and they would no longer be found on Earth. Because they are generated continuously by the decay of uranium or thorium, however, their amounts have reached a steady state, in which their rate of formation is equal to their rate of decay. In some cases, the abundance of the daughter isotopes can be used to date a material or identify its origin.

Induced Nuclear Reactions

The discovery of radioactivity in the late 19th century showed that some nuclei spontaneously transform into nuclei with a different number of protons, thereby producing a different element. When scientists realized that these naturally occurring radioactive isotopes decayed by emitting subatomic particles, they realized that—in principle—it should be possible to carry out the reverse reaction, converting a stable nucleus to another more massive nucleus by bombarding it with subatomic particles in a nuclear transmutation reaction.

The first successful nuclear transmutation reaction was carried out in 1919 by Ernest Rutherford, who showed that α particles emitted by radium could react with nitrogen nuclei to form oxygen nuclei. As shown in the following equation, a proton is emitted in the process:

$$ {}^{4}_{2}\alpha + {}^{14}_{7}\mathrm{N} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p} $$

Rutherford's nuclear transmutation experiments led to the discovery of the neutron. He found that bombarding the nucleus of a light target element with an α particle usually converted the target nucleus to a product that had an atomic number higher by 1 and a mass number higher by 3 than the target nucleus. Such behavior is consistent with the emission of a proton after reaction with the α particle. Very light targets such as Li, Be, and B reacted differently, however, emitting a new kind of highly penetrating radiation rather than a proton. Because neither a magnetic field nor an electrical field could deflect these high-energy particles, Rutherford concluded that they were electrically neutral. Other observations suggested that the mass of the neutral particle was similar to the mass of the proton. In 1932, James Chadwick (Nobel Prize in Physics, 1935), who was a student of Rutherford's at the time, named these neutral particles neutrons and proposed that they were fundamental building blocks of the atom. The reaction that Chadwick initially used to explain the production of neutrons was as follows:

$$ {}^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{21.1.8} $$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure 21.1.3). Neutrons have no

electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

$$^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{21.1.9}$$

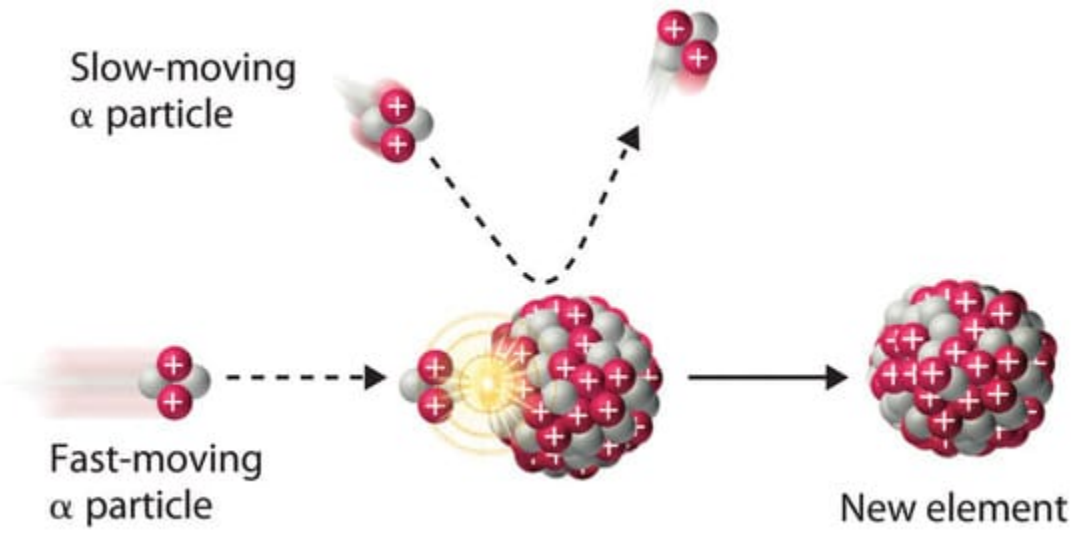


Figure 21.1.3: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.

Example 21.1.4

In 1933, Frédéric Joliot and Iréne Joliot-Curie (daughter of Marie and Pierre Curie) prepared the first artificial radioactive isotope by bombarding aluminum-27 with α particles. For each ^{27}Al that reacted, one neutron was released. Identify the product nuclide and write a balanced nuclear equation for this transmutation reaction.

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

A Based on the reactants and one product, identify the other product of the reaction. Use conservation of mass and charge to determine the values of *Z* and *A* of the product nuclide and thus its identity.

B Write the balanced nuclear equation for the reaction.

Solution

A Bombarding an element with α particles usually produces an element with an atomic number that is 2 greater than the atomic number of the target nucleus. Thus we expect that aluminum (*Z* = 13) will be converted to phosphorus (*Z* = 15). With one neutron released, conservation of mass requires that the mass number of the other product be 3 greater than the mass number of the target. In this case, the mass number of the target is 27, so the mass number of the product will be 30. The second product is therefore phosphorus-30, $^{30}_{15}\mathrm{P}$.

B The balanced nuclear equation for the reaction is as follows:

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\alpha \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n}$$

Exercise 21.1.4

Because all isotopes of technetium are radioactive and have short half-lives, it does not exist in nature. Technetium can, however, be prepared by nuclear transmutation reactions. For example, bombarding a molybdenum-96 target with deuterium nuclei ($^{2}_{1}\mathrm{H}$) produces technetium-97. Identify the other product of the reaction and write a balanced nuclear equation for this transmutation reaction.

Answer available at the end of this section.

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of Z, such as the isotopes of uranium (Z = 92) and plutonium (Z = 94), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as $^{235}_{92}\mathrm{U}$ and $^{239}_{94}\mathrm{Pu}$ undergo induced nuclear fission when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure 21.1.4:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{21.1.10}$$

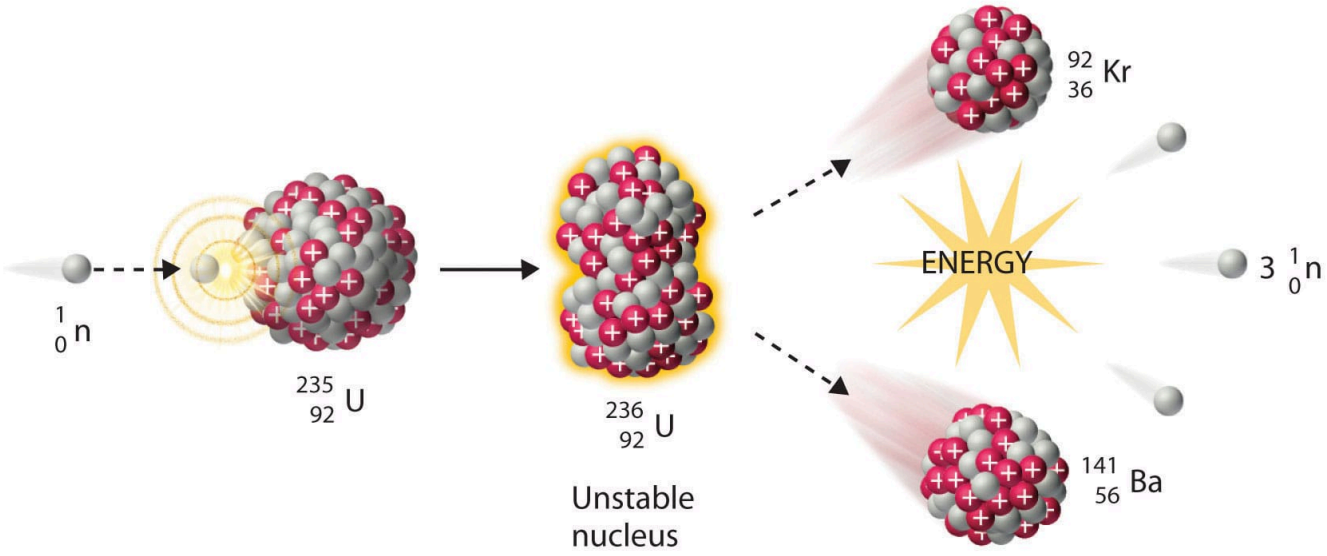


Figure 21.1.4 Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

Any isotope that can undergo a nuclear fission reaction when bombarded with neutrons is called a **fissile isotope**.

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure 21.1.4. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure 21.1.5, a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

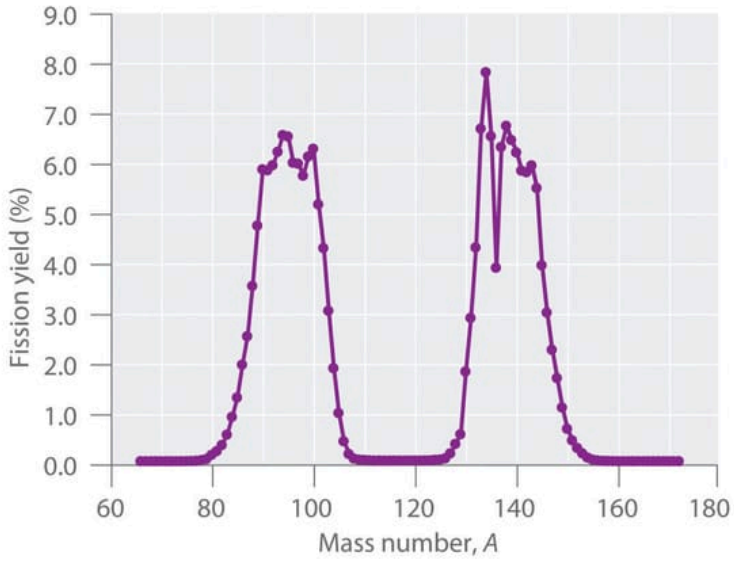


Figure 21.1.5: Mass Distribution of Nuclear Fission Products of ^{235}U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for ^{235}U. Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

Synthesis of Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with Z > 92, the **transuranium elements**, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation 20.21, this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 21.1.2). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability."

Table 21.1.2: Some Reactions Used to Synthesize Transuranium Elements

$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{241}_{95}\mathrm{Am} + {}^{1}_{1}\mathrm{p} + {}^{1}_{0}\mathrm{n}$
$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\alpha \rightarrow {}^{243}_{97}\mathrm{Bk} + {}^{1}_{1}\mathrm{p} + 2{}^{1}_{0}\mathrm{n}$
$^{253}_{99}\mathrm{Es} + {}^{4}_{2}\alpha \rightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$
$^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{246}_{98}\mathrm{Cf} + 4{}^{1}_{0}\mathrm{n}$
$^{252}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \rightarrow {}^{256}_{103}\mathrm{Lr} + 6{}^{1}_{0}\mathrm{n}$

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 21.1.6), in which a beam of particles is injected at one end of a long evacuated

tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

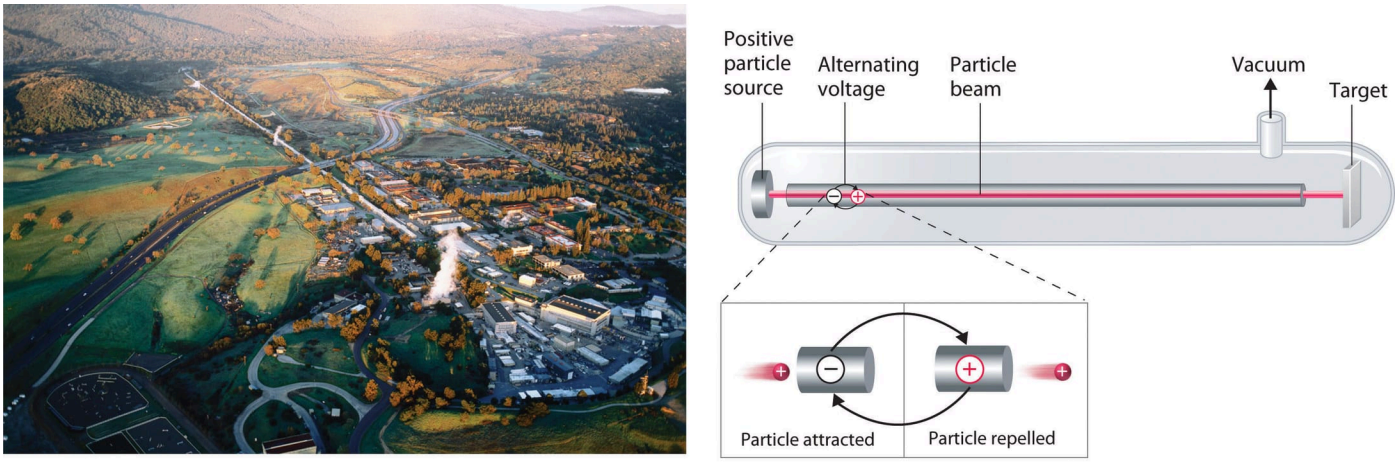


Figure 21.1.6: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

To achieve the same outcome in less space, a particle accelerator called a cyclotron forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

The length of a linear accelerator and the size of the D-shaped electrodes in a cyclotron severely limit the kinetic energy that particles can attain in these devices. These limitations can be overcome by using a synchrotron, a hybrid of the two designs. A synchrotron contains an evacuated tube similar to that of a linear accelerator, but the tube is circular and can be more than a mile in diameter. Charged particles are accelerated around the circle by a series of magnets whose polarities rapidly alternate.

Summary and Key Takeaway

- Nuclear decay reactions occur spontaneously under all conditions and produce more stable daughter nuclei, whereas nuclear transmutation reactions are induced and form a product nucleus that is more massive than the starting material.

In **nuclear decay reactions (or radioactive decay)**, the parent nucleus is converted to a more stable daughter nucleus. Nuclei with too many neutrons decay by converting a neutron to a proton, whereas nuclei with too few neutrons decay by converting a proton to a neutron. Very heavy nuclei (with $A \geq 200$ and $Z > 83$) are unstable and tend to decay by emitting an **α particle**. When an unstable nuclide undergoes radioactive decay, the total number of nucleons is conserved, as is the total positive charge. Six different kinds of nuclear decay reactions are known. *Alpha decay* results in the emission of an α particle, ${}^{4}_{2}\alpha$, and produces a daughter nucleus with a mass number that is lower by 4 and an atomic number that is lower by 2 than the parent nucleus. **Beta decay** converts a neutron to a proton and emits a high-energy electron, producing a daughter nucleus with the same mass number as the parent and an atomic number that is higher by 1. **Positron emission** is the opposite of beta decay and converts a proton to a neutron plus a positron. Positron emission does not change the mass number of the nucleus, but the atomic number of the daughter nucleus is lower by 1 than the parent. In **electron capture (EC)**, an electron in an inner shell reacts with a proton to produce a neutron, with emission of an x-ray. The mass number does not change, but the atomic number of the daughter is lower by 1 than the parent. In **gamma emission**, a daughter nucleus in a nuclear excited state undergoes a transition to a lower-energy state by emitting a γ ray. Very heavy nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that can have different atomic numbers and atomic masses with the release of neutrons. Many very heavy nuclei decay via a **radioactive decay series**—a succession of some combination of alpha- and beta-decay reactions. In **nuclear transmutation reactions**, a target nucleus is bombarded with energetic subatomic particles to give a product nucleus that is more massive than the original. All **transuranium elements**—elements with $Z > 92$—are artificial and must be prepared by

nuclear transmutation reactions. These reactions are carried out in particle accelerators such as linear accelerators, cyclotrons, and synchrotrons.

Key Equations

alpha decay

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^{4}_{2}\alpha $$

beta decay

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z+1}\mathrm{X}' + {}^{0}_{-1}\beta $$

positron emission

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + {}^{0}_{+1}\beta $$

electron capture

$$ {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + \text{x-ray} $$

gamma emission

$$ {}^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma $$

Answers

Exercise 21.1.1

$$ {}^{125}_{53}\mathrm{I} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{125}_{52}\mathrm{Te} $$

Exercise 21.1.2

${}^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta$

${}^{99}_{42}\mathrm{Mo} \rightarrow {}^{99m}_{43}\mathrm{Tc} + {}^{0}_{-1}\beta$

${}^{185}_{74}\mathrm{W} \rightarrow {}^{181}_{72}\mathrm{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$

Exercise 21.1.3

beta decay

positron emission or electron capture

alpha decay

Exercise 21.1.4

neutron, ${}^{1}_{0}\mathrm{n}$; ${}^{96}_{42}\mathrm{Mo} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{97}_{43}\mathrm{Tc} + {}^{1}_{0}\mathrm{n}$:

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21.2: Patterns of Nuclear Stability

Learning Objectives

- To understand the factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or decay, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that were the main focus of earlier chapters and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

The Atomic Nucleus

Each element can be represented by the notation ${}^{A}_{Z}\mathrm{X}$, where *A*, the mass number, is the sum of the number of protons and the number of neutrons, and *Z*, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are called **nucleons**, and an atom with a particular number of protons and neutrons is called a **nuclide**. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

stable isotopes of oxygen represented in different ways

${}^{A}_{Z}\mathrm{X}$	${}^{16}_{8}\mathrm{O}$	${}^{17}_{8}\mathrm{O}$	${}^{18}_{8}\mathrm{O}$
${}^{A}\mathrm{X}$	${}^{16}\mathrm{O}$	${}^{17}\mathrm{O}$	${}^{18}\mathrm{O}$
element-A:	oxygen-16	oxygen-17	oxygen-18

Because the number of neutrons is equal to *A* – *Z*, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17. Any nucleus that is unstable and decays spontaneously is said to be **radioactive**, emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called **radioisotopes**.

Nuclear Stability

The nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the **strong nuclear force**, an extremely powerful but very short-range attractive force between nucleons (Figure 21.2.1). All stable nuclei except the hydrogen-1 nucleus (${}^{1}\mathrm{H}$) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

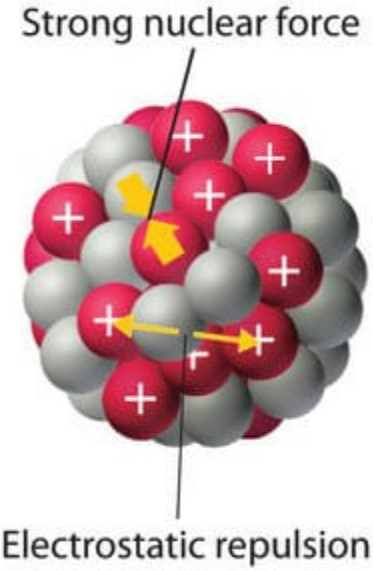


Figure 21.2.1: Competing Interactions within the Atomic Nucleus. Electrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure 21.2.2. The stable isotopes form a "peninsula of stability" in a "sea of instability." Only two stable isotopes, ^{1}H and ^{3}He, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., $^{4}_{2}\mathrm{He}$, $^{10}_{5}\mathrm{B}$, and $^{40}_{20}\mathrm{Ca}$). All other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with Z > 83 are unstable and radioactive.

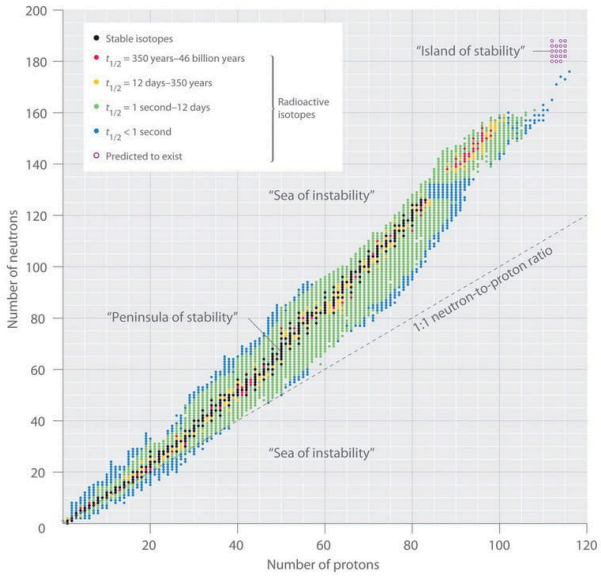


Figure 21.2.2: The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio. In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized. Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides, http://www.nndc.bnl.gov/chart.

Graph of number or neutrons against the number or protons. The graph is divided into sections of "sea of instability", "peninsula of stability", "sea of instability" and "island of stability"

As shown in Figure 21.2.3, more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in especially stable nuclei; these are the so-called *magic numbers* 2, 8, 20, 50, 82, and 126. For example, tin (Z = 50) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium (Z = 49) and antimony (Z = 51), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be “doubly magic” and are even more stable. Examples of elements with doubly magic nuclei are $^{4}_{2}\mathrm{He}$, with 2 protons and 2 neutrons, and $^{208}_{82}\mathrm{Pb}$, with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

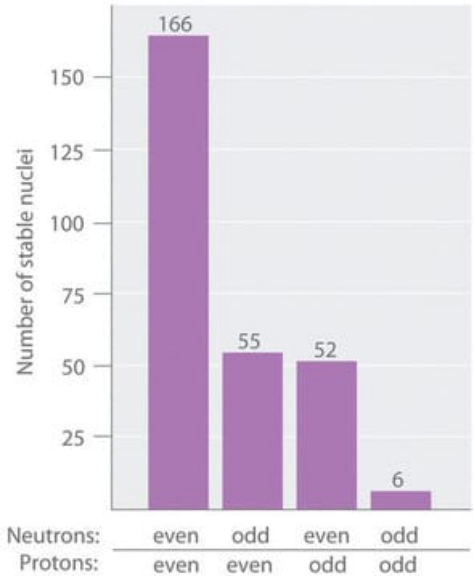


Figure 21.2.3: The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability.

Most stable nuclei contain **even** numbers of both neutrons and protons

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure 21.2.2, the "peninsula" of stable isotopes is surrounded by a "reef" of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

Origin of the Magic Numbers

Multiple models have been formulated to explain the origin of the magic numbers and two popular ones are the Nuclear Shell Model and the Liquid Drop Model. Unfortuneatly, both require advanced quantum mechanics to fully understand and are beyond the scope of this text.

Example 21.2.1

Classify each nuclide as stable or radioactive.

a. $^{30}_{15}\mathrm{P}$
b. $^{98}_{43}\mathrm{Tc}$
c. tin-118
d. $^{239}_{94}\mathrm{Pu}$

Given: mass number and atomic number

Asked for: predicted nuclear stability

Strategy:

Use the number of protons, the neutron-to-proton ratio, and the presence of even or odd numbers of neutrons and protons to predict the stability or radioactivity of each nuclide.

Solution:

a. This isotope of phosphorus has 15 neutrons and 15 protons, giving a neutron-to-proton ratio of 1.0. Although the atomic number, 15, is much less than the value of 83 above which all nuclides are unstable, the neutron-to-proton ratio is less than that expected for stability for an element with this mass. As shown in Figure 21.2.2, its neutron-to-proton ratio should be greater than 1. Moreover, this isotope has an odd number of both neutrons and protons, which also tends to make a nuclide unstable. Consequently, $^{30}_{15}\mathrm{P}$ is predicted to be radioactive, and it is.

b. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which places $^{98}_{43}\mathrm{Tc}$ near the edge of the band of stability. The atomic number, 55, is much less than the value of 83 above which all isotopes are unstable. These facts suggest that $^{98}_{43}\mathrm{Tc}$ might be stable. However, $^{98}_{43}\mathrm{Tc}$ has an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, $^{98}_{43}\mathrm{Tc}$ is predicted to be radioactive, and it is.

c. Tin-118 has 68 neutrons and 50 protons, for a neutron-to-proton ratio of 1.36. As in part b, this value and the atomic number both suggest stability. In addition, the isotope has an even number of both neutrons and protons, which tends to increase nuclear stability. Most important, the nucleus has 50 protons, and 50 is one of the magic numbers associated with especially stable nuclei. Thus $^{118}_{50}\mathrm{Sn}$should be particularly stable.

d. This nuclide has an atomic number of 94. Because all nuclei with Z > 83 are unstable, $^{239}_{94}\mathrm{Pu}$ must be radioactive.

Exercise 21.2.1

Classify each nuclide as stable or radioactive.

a. $^{232}_{90}\mathrm{Th}$
b. $^{40}_{20}\mathrm{Ca}$
c. $^{15}_{8}\mathrm{O}$
d. $^{139}_{57}\mathrm{La}$

Answer a available at the end of this section.

Superheavy Elements

In addition to the “peninsula of stability” there is a small “island of stability” that is predicted to exist in the upper right corner. This island corresponds to the **superheavy elements**, with atomic numbers near the magic number 126. Because the next magic number for neutrons should be 184, it was suggested that an element with 114 protons and 184 neutrons might be stable enough to exist in nature. Although these claims were met with skepticism for many years, since 1999 a few atoms of isotopes with Z = 114 and Z = 116 have been prepared and found to be surprisingly stable. One isotope of element 114 lasts 2.7 seconds before decaying, described as an “eternity” by nuclear chemists. Moreover, there is recent evidence for the existence of a nucleus with A = 292 that was found in ^{232}Th. With an estimated half-life greater than 10^8 years, the isotope is particularly stable. Its measured mass is consistent with predictions for the mass of an isotope with Z = 122. Thus a number of relatively long-lived nuclei may well be accessible among the superheavy elements.

Summary

Subatomic particles of the nucleus (protons and neutrons) are called **nucleons**. A **nuclide** is an atom with a particular number of protons and neutrons. An unstable nucleus that decays spontaneously is **radioactive**, and its emissions are collectively called *radioactivity*. Isotopes that emit radiation are called **radioisotopes**. Each nucleon is attracted to other nucleons by the **strong nuclear force**. Stable nuclei generally have even numbers of both protons and neutrons and a neutron-to-proton ratio of at least 1. Nuclei that contain *magic numbers* of protons and neutrons are often especially stable. **Superheavy elements**, with atomic numbers near 126, may even be stable enough to exist in nature.

Answers

Exercise 21.2.1

radioactive
stable
radioactive
stable

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21.3: Nuclear Transmutations

Learning Objectives

- To understand how nuclear transmutation reactions lead to the formation of the elements in stars and how they can be used to synthesize transuranium elements.

The relative abundances of the elements in the known universe vary by more than 12 orders of magnitude. For the most part, these differences in abundance cannot be explained by differences in nuclear stability. Although the ^{56}Fe nucleus is the most stable nucleus known, the most abundant element in the known universe is not iron, but hydrogen (^{1}H), which accounts for about 90% of all atoms. In fact, ^{1}H is the raw material from which all other elements are formed. In this section, we explain why ^{1}H and ^{2}He together account for at least 99% of all the atoms in the known universe. We also describe the nuclear reactions that take place in stars, which transform one nucleus into another and create all the naturally occurring elements.

Relative Abundances of the Elements on Earth and in the Known Universe

The relative abundances of the elements in the known universe and on Earth relative to silicon are shown in Figure 21.3.1. The data are estimates based on the characteristic emission spectra of the elements in stars, the absorption spectra of matter in clouds of interstellar dust, and the approximate composition of Earth as measured by geologists. The data in Figure 21.3.1 illustrate two important points. First, except for hydrogen, the most abundant elements have even atomic numbers. Not only is this consistent with the known trends in nuclear stability, but it also suggests that heavier elements are formed by combining helium nuclei (Z = 2). Second, the relative abundances of the elements in the known universe and on Earth are often very different, as indicated by the data in Table 21.3.1 for some common elements.

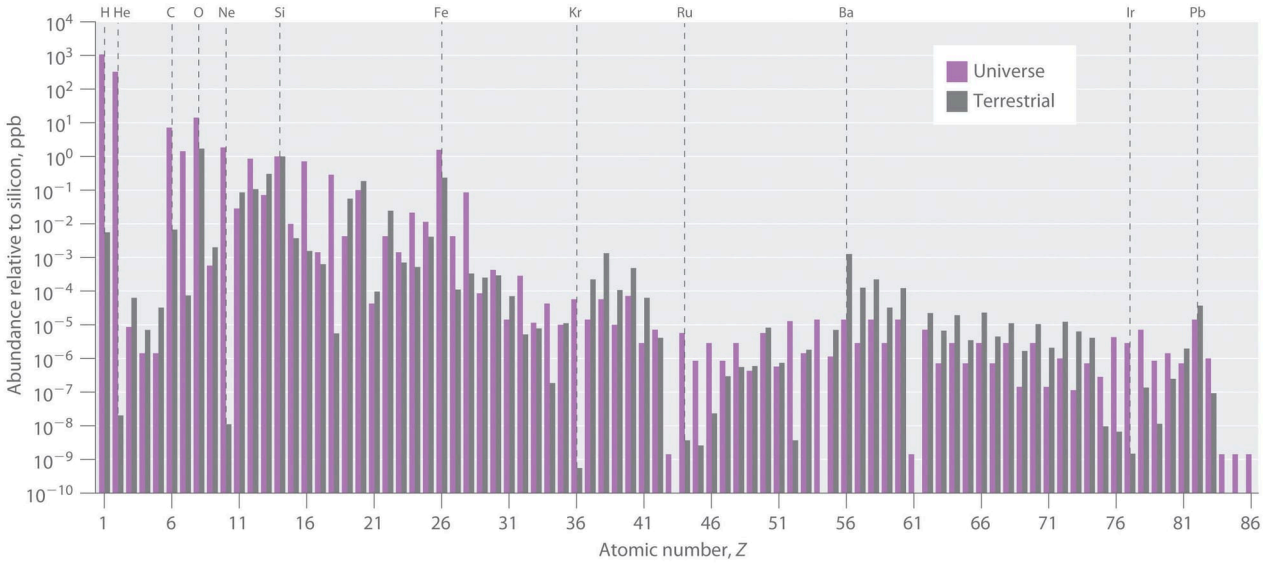


Figure 21.3.1: The Relative Abundances of the Elements in the Universe and on Earth. In this logarithmic plot, the relative abundances of the elements relative to that of silicon (arbitrarily set equal to 1) in the universe (green bars) and on Earth (purple bars) are shown as a function of atomic number. Elements with even atomic numbers are generally more abundant in the universe than elements with odd atomic numbers. Also, the relative abundances of many elements in the universe are very different from their relative abundances on Earth. (CC BY-NC-SA 3.0; anonymous)

Bar graph of abundance realtive to silicon in pbb against atomic number. The purple bars are universe elements while the gray bars are terrestrial elements.

Some of these differences are easily explained. For example, nonmetals such as H, He, C, N, O, Ne, and Kr are much less abundant relative to silicon on Earth than they are in the rest of the universe. These elements are either noble gases (He, Ne, and Kr) or

elements that form volatile hydrides, such as NH_3, CH_4, and H_2O. Because Earth's gravity is not strong enough to hold such light substances in the atmosphere, these elements have been slowly diffusing into outer space ever since our planet was formed. Argon is an exception; it is relatively abundant on Earth compared with the other noble gases because it is continuously produced in rocks by the radioactive decay of isotopes such as ^{40}K. In contrast, many metals, such as Al, Na, Fe, Ca, Mg, K, and Ti, are relatively abundant on Earth because they form nonvolatile compounds, such as oxides, that cannot escape into space. Other metals, however, are much less abundant on Earth than in the universe; some examples are Ru and Ir. This section explains some of the reasons for the great differences in abundances of the metallic elements.

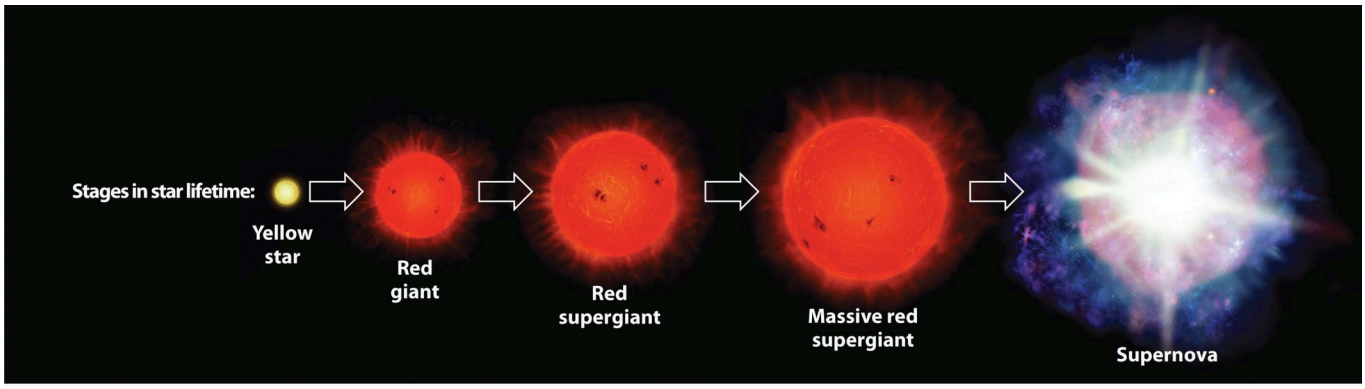
Table 21.3.1: Relative Abundances of Elements on Earth and in the Known Universe

Terrestrial/Universal Element	Abundance Ratio
H	0.0020
He	2.4×10^{-8}
C	0.36
N	0.02
O	46
Ne	1.9×10^{-6}
Na	1200
Mg	48
Al	1600
Si	390
S	0.84
K	5000
Ca	710
Ti	2200
Fe	57

All the elements originally present on Earth (and on other planets) were synthesized from hydrogen and helium nuclei in the interiors of stars that have long since exploded and disappeared. Six of the most abundant elements in the universe (C, O, Ne, Mg, Si, and Fe) have nuclei that are integral multiples of the helium-4 nucleus, which suggests that helium-4 is the primary building block for heavier nuclei.

Synthesis of the Elements in Stars

Elements are synthesized in discrete stages during the lifetime of a star, and some steps occur only in the most massive stars known (Figure 21.3.2). Initially, all stars are formed by the aggregation of interstellar "dust," which is mostly hydrogen. As the cloud of dust slowly contracts due to gravitational attraction, its density eventually reaches about 100 g/cm^3, and the temperature increases to about 1.5×10^7 K, forming a dense plasma of ionized hydrogen nuclei. At this point, self-sustaining nuclear reactions begin, and the star "ignites," creating a yellow star like our sun.



Core Temperature:	1.5×10^7 K	2×10^8 K	7×10^8 K	3×10^9 K	1×10^{11} K
Primary Nuclear Reaction:	^{1}H fusion	^{4}He fusion	$^4\text{He} + {}^{12}\text{C}$ $^{12}\text{C} + {}^{12}\text{C}$ $^{12}\text{C} + {}^{16}\text{O}$	Proton–neutron exchange reactions	Multiple neutron captures
Elements Formed:	He	C, O, Ne, Mg	Na, Si, S, Ar, Ca	Fe, Ni	Elements with $Z > 28$

Figure 21.3.2: Nuclear Reactions during the Life Cycle of a Massive Star. At each stage in the lifetime of a star, a different fuel is used for nuclear fusion, resulting in the formation of different elements. Fusion of hydrogen to give helium is the primary fusion reaction in young stars. As the star ages, helium accumulates and begins to "burn," undergoing fusion to form heavier elements such as carbon and oxygen. As the adolescent star matures, significant amounts of iron and nickel are formed by fusion of the heavier elements formed previously. The heaviest elements are formed only during the final death throes of the star—the formation of a nova or supernova.

The stages in a stare lifetime are yellow star, red giant, red supergiant, massive red supergiant and finally supernova.

In the first stage of its life, the star is powered by a series of nuclear fusion reactions that convert hydrogen to helium:

$$\begin{aligned} {}^1_1\text{H} + {}^1_1\text{H} &\rightarrow {}^2_1\text{H} + {}^0_{+1}\beta \\ {}^2_1\text{H} + {}^1_1\text{H} &\rightarrow {}^3_2\text{He} + {}^0_0\gamma \\ {}^3_2\text{He} + {}^3_2\text{He} &\rightarrow {}^4_2\text{He} + 2{}^1_1\text{H} \end{aligned} \tag{21.3.1}$$

The overall reaction is the conversion of four hydrogen nuclei to a helium-4 nucleus, which is accompanied by the release of two positrons, two γ rays, and a great deal of energy:

$$4{}^1_1\text{H} \rightarrow {}^4_2\text{He} + 2{}^0_{+1}\beta + 2{}^0_0\gamma \tag{21.3.2}$$

These reactions are responsible for most of the enormous amount of energy that is released as sunlight and solar heat. It takes several billion years, depending on the size of the star, to convert about 10% of the hydrogen to helium.

Once large amounts of helium-4 have been formed, they become concentrated in the core of the star, which slowly becomes denser and hotter. At a temperature of about 2×10^8 K, the helium-4 nuclei begin to fuse, producing beryllium-8:

$$2{}^4_2\text{He} \rightarrow {}^8_4\text{Be} \tag{21.3.3}$$

Although beryllium-8 has both an even mass number and an even atomic number, its also has a low neutron-to-proton ratio (and other factors beyond the scope of this text) that makes it unstable; it decomposes in only about 10^{-16} s. Nonetheless, this is long enough for it to react with a third helium-4 nucleus to form carbon-12, which is very stable. Sequential reactions of carbon-12 with helium-4 produce the elements with even numbers of protons and neutrons up to magnesium-24:

$${}^8_4\text{Be} \xrightarrow{{}^4_2\text{He}} {}^{12}_6\text{C} \xrightarrow{{}^4_2\text{He}} {}^{16}_8\text{O} \xrightarrow{{}^4_2\text{He}} {}^{20}_{10}\text{Ne} \xrightarrow{{}^4_2\text{He}} {}^{24}_{12}\text{Mg} \tag{21.3.4}$$

So much energy is released by these reactions that it causes the surrounding mass of hydrogen to expand, producing a red giant that is about 100 times larger than the original yellow star.

As the star expands, heavier nuclei accumulate in its core, which contracts further to a density of about 50,000 g/cm3, so the core becomes even hotter. At a temperature of about 7×10^8 K, carbon and oxygen nuclei undergo nuclear fusion reactions to produce sodium and silicon nuclei:

$$^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{23}_{11}\mathrm{Na} + {}^{1}_{1}\mathrm{H} \tag{21.3.5}$$

$$^{12}_{6}\mathrm{C} + {}^{16}_{8}\mathrm{O} \rightarrow {}^{28}_{14}\mathrm{Si} + {}^{0}_{0}\gamma \tag{21.3.6}$$

At these temperatures, carbon-12 reacts with helium-4 to initiate a series of reactions that produce more oxygen-16, neon-20, magnesium-24, and silicon-28, as well as heavier nuclides such as sulfur-32, argon-36, and calcium-40:

$$^{12}_{6}\mathrm{C} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{16}_{8}\mathrm{O} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{20}_{10}\mathrm{Ne} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{24}_{12}\mathrm{Mg} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{28}_{14}\mathrm{Si} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{32}_{16}\mathrm{S} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{36}_{18}\mathrm{Ar} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{40}_{20}\mathrm{Ca} \tag{21.3.7}$$

The energy released by these reactions causes a further expansion of the star to form a red supergiant, and the core temperature increases steadily. At a temperature of about 3×10^9 K, the nuclei that have been formed exchange protons and neutrons freely. This equilibration process forms heavier elements up to iron-56 and nickel-58, which have the most stable nuclei known.

The Formation of Heavier Elements in Supernovas

None of the processes described so far produces nuclei with Z > 28. All naturally occurring elements heavier than nickel are formed in the rare but spectacular cataclysmic explosions called supernovas (Figure 21.3.2). When the fuel in the core of a very massive star has been consumed, its gravity causes it to collapse in about 1 s. As the core is compressed, the iron and nickel nuclei within it disintegrate to protons and neutrons, and many of the protons capture electrons to form neutrons. The resulting neutron star is a dark object that is so dense that atoms no longer exist. Simultaneously, the energy released by the collapse of the core causes the supernova to explode in what is arguably the single most violent event in the universe. The force of the explosion blows most of the star's matter into space, creating a gigantic and rapidly expanding dust cloud, or nebula (Figure 21.3.3). During the extraordinarily short duration of this event, the concentration of neutrons is so great that multiple neutron-capture events occur, leading to the production of the heaviest elements and many of the less stable nuclides. Under these conditions, for example, an iron-56 nucleus can absorb as many as 64 neutrons, briefly forming an extraordinarily unstable iron isotope that can then undergo multiple rapid β-decay processes to produce tin-120:

$$^{56}_{26}\mathrm{Fe} + 64\,^{1}_{0}\mathrm{n} \rightarrow {}^{120}_{26}\mathrm{Fe} \rightarrow {}^{120}_{50}\mathrm{Sn} + 24\,^{0}_{-1}\beta \tag{21.3.8}$$



Figure 21.3.3: A Supernova. A view of the remains of Supernova 1987A, located in the Large Magellanic Cloud, showing the circular halo of expanding debris produced by the explosion. Multiple neutron-capture events occur during a supernova explosion, forming both the heaviest elements and many of the less stable nuclides.

Although a supernova occurs only every few hundred years in a galaxy such as the Milky Way, these rare explosions provide the only conditions under which elements heavier than nickel can be formed. The force of the explosions distributes these elements throughout the galaxy surrounding the supernova, and eventually they are captured in the dust that condenses to form new stars. Based on its elemental composition, our sun is thought to be a second- or third-generation star. It contains a considerable

amount of cosmic debris from the explosion of supernovas in the remote past.

Example 21.3.1: Carbon Burning Stars

The reaction of two carbon-12 nuclei in a carbon-burning star can produce elements other than sodium. Write a balanced nuclear equation for the formation of

a. magnesium-24.
b. neon-20 from two carbon-12 nuclei.

Given: reactant and product nuclides

Asked for: balanced nuclear equation

Strategy:

Use conservation of mass and charge to determine the type of nuclear reaction that will convert the reactant to the indicated product. Write the balanced nuclear equation for the reaction.

Solution

a. A magnesium-24 nucleus (Z = 12, A = 24) has the same nucleons as two carbon-12 nuclei (Z = 6, A = 12). The reaction is therefore a fusion of two carbon-12 nuclei, and no other particles are produced: ${}^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{24}_{12}\mathrm{Mg}$.
b. The neon-20 product has Z = 10 and A = 20. The conservation of mass requires that the other product have A = (2 × 12) – 20 = 4; because of conservation of charge, it must have Z = (2 × 6) – 10 = 2. These are the characteristics of an α particle. The reaction is therefore ${}^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{20}_{10}\mathrm{Ne} + {}^{4}_{2}\alpha$.

Exercise 21.3.1

How many neutrons must an iron-56 nucleus absorb during a supernova explosion to produce an arsenic-75 nucleus? Write a balanced nuclear equation for the reaction.

Answer available at the end of this section.

Summary

Hydrogen and helium are the most abundant elements in the universe. Heavier elements are formed in the interior of stars via multiple neutron-capture events. By far the most abundant element in the universe is hydrogen. The fusion of hydrogen nuclei to form helium nuclei is the major process that fuels young stars such as the sun. Elements heavier than helium are formed from hydrogen and helium in the interiors of stars. Successive fusion reactions of helium nuclei at higher temperatures create elements with even numbers of protons and neutrons up to magnesium and then up to calcium. Eventually, the elements up to iron-56 and nickel-58 are formed by exchange processes at even higher temperatures. Heavier elements can only be made by a process that involves multiple neutron-capture events, which can occur only during the explosion of a supernova.

Answers

Exercise 21.3.1

19 neutrons; ${}^{56}_{26}\mathrm{Fe} + 19{}^{1}_{0}\mathrm{n} \rightarrow {}^{75}_{26}\mathrm{Fe} \rightarrow {}^{75}_{33}\mathrm{As} + 7{}^{0}_{-1}\beta$

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21.4: Rates of Radioactive Decay

Learning Objectives

- To know how to use half-lives to describe the rates of first-order reactions

Another approach to describing reaction rates is based on the time required for the concentration of a reactant to decrease to one-half its initial value. This period of time is called the **half-life** of the reaction, written as $t_{1/2}$. Thus the half-life of a reaction is the time required for the reactant concentration to decrease from $[A]_0$ to $[A]_{0/2}$. If two reactions have the same order, the faster reaction will have a shorter half-life, and the slower reaction will have a longer half-life.

The half-life of a first-order reaction under a given set of reaction conditions is a constant. This is not true for zeroth- and second-order reactions. The half-life of a first-order reaction is independent of the concentration of the reactants. This becomes evident when we rearrange the integrated rate law for a first-order reaction to produce the following equation:

$$\ln \frac{[A]_0}{[A]} = kt \tag{21.4.1}$$

Substituting $[A]_{0/2}$ for [A] and $t_{1/2}$ for t (to indicate a half-life) into Equation 21.4.1 gives

$$\ln \frac{[A]_0}{[A]_0/2} = \ln 2 = kt_{1/2} \tag{21.4.2}$$

Substituting $\ln 2 \approx 0.693$ into the equation results in the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \tag{21.4.3}$$

Thus, for a first-order reaction, each successive half-life is the same length of time, as shown in Figure 21.4.1, and is *independent* of [A].

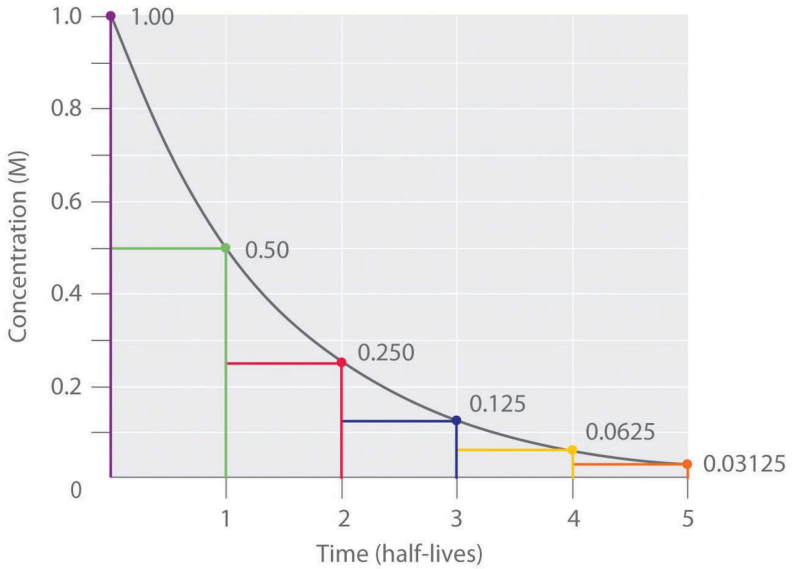


Figure 21.4.1: The Half-Life of a First-Order Reaction. This plot shows the concentration of the reactant in a first-order reaction as a function of time and identifies a series of half-lives, intervals in which the reactant concentration decreases by a factor of 2. In a first-order reaction, every half-life is the same length of time.

If we know the rate constant for a first-order reaction, then we can use half-lives to predict how much time is needed for the reaction to reach a certain percent completion.

Number of Half-Lives	Percentage of Reactant Remaining	
1	$\frac{100\%}{2} = 50\%$	$\frac{1}{2}(100\%) = 50\%$
2	$\frac{50\%}{2} = 25\%$	$\frac{1}{2}\left(\frac{1}{2}\right)(100\%) = 25\%$
3	$\frac{25\%}{2} = 12.5\%$	$\frac{1}{2}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(100\%) = 12.5\%$
n	$\frac{100\%}{2^n}$	$\left(\frac{1}{2}\right)^n(100\%) = \left(\frac{1}{2}\right)^n\%$

As you can see from this table, the amount of reactant left after *n* half-lives of a first-order reaction is $(1/2)^n$ times the initial concentration.

For a first-order reaction, the concentration of the reactant decreases by a constant with each half-life and is independent of [A].

Example 21.4.1

The anticancer drug cis-platin hydrolyzes in water with a rate constant of 1.5×10^{-3} min^{-1} at pH 7.0 and 25°C. Calculate the half-life for the hydrolysis reaction under these conditions. If a freshly prepared solution of cis-platin has a concentration of 0.053 M, what will be the concentration of cis-platin after 5 half-lives? after 10 half-lives? What is the percent completion of the reaction after 5 half-lives? after 10 half-lives?

Given: rate constant, initial concentration, and number of half-lives

Asked for: half-life, final concentrations, and percent completion

Strategy:

A. Use Equation 21.4.3 to calculate the half-life of the reaction.
B. Multiply the initial concentration by 1/2 to the power corresponding to the number of half-lives to obtain the remaining concentrations after those half-lives.
C. Subtract the remaining concentration from the initial concentration. Then divide by the initial concentration, multiplying the fraction by 100 to obtain the percent completion.

Solution A

We can calculate the half-life of the reaction using Equation 21.4.3:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-3}\ \text{min}^{-1}} = 4.6 \times 10^2\ \text{min}$$

Thus it takes almost 8 h for half of the cis-platin to hydrolyze.

Solution B

fter 5 half-lives (about 38 h), the remaining concentration of cis-platin will be as follows:

$$\frac{0.053\ \text{M}}{2^5} = \frac{0.053\ \text{M}}{32} = 0.0017\ \text{M}$$

After 10 half-lives (77 h), the remaining concentration of cis-platin will be as follows:

$$\frac{0.053\ \text{M}}{2^{10}} = \frac{0.053\ \text{M}}{1024} = 5.2 \times 10^{-5}\ \text{M}$$

Solution C

The percent completion after 5 half-lives will be as follows:

$$\text{percent completion} = \frac{(0.053\ \text{M} - 0.0017\ \text{M})(100)}{0.053} = 97\%$$

The percent completion after 10 half-lives will be as follows:

$$\text{percent completion} = \frac{(0.053\ \text{M} - 5.2 \times 10^{-5}\ \text{M})(100)}{0.053\ \text{M}} = 100\%$$

Thus a first-order chemical reaction is 97% complete after 5 half-lives and 100% complete after 10 half-lives.

Exercise 21.4.1

Ethyl chloride decomposes to ethylene and HCl in a first-order reaction that has a rate constant of $1.6 \times 10^{-6}\ \text{s}^{-1}$ at 650°C.

a. What is the half-life for the reaction under these conditions?
b. If a flask that originally contains 0.077 M ethyl chloride is heated at 650°C, what is the concentration of ethyl chloride after 4 half-lives?

Answer a available at the end of this section.

Radioactive Decay Rates

Radioactivity, or radioactive decay, is the emission of a particle or a photon that results from the spontaneous decomposition of the unstable nucleus of an atom. The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. In this section, we will describe radioactive decay rates and how half-lives can be used to monitor radioactive decay processes.

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using *N* to represent the number of atoms of the radioactive isotope, we can define the **rate of decay** of the sample, which is also called its **activity (*A*)** as the decrease in the number of the radioisotope's nuclei per unit time:

$$A = -\frac{\Delta N}{\Delta t} \tag{21.4.4}$$

Activity is usually measured in disintegrations per second (dps) or disintegrations per minute (dpm).

The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = kN \tag{21.4.5}$$

Here, the symbol *k* is the radioactive decay constant, which has units of inverse time (e.g., s^{-1}, yr^{-1}) and a characteristic value for each radioactive isotope. If we combine Equation 21.4.4 and Equation 21.4.5, we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{\Delta N}{\Delta t} = kN \tag{21.4.6}$$

Equation 21.4.6 is the same as the equation for the reaction rate of a first-order reaction, except that it uses numbers of atoms instead of concentrations. In fact, radioactive decay is a first-order process and can be described in terms of either the differential rate law (Equation 21.4.6) or the integrated rate law:

$$N = N_0 e^{-kt} \tag{21.4.7}$$

$$\ln \frac{N}{N_0} = -kt \tag{21.4.8}$$

Because radioactive decay is a first-order process, the time required for half of the nuclei in any sample of a radioactive isotope to decay is a constant, called the half-life of the isotope. The half-life tells us how radioactive an isotope is (the number of decays per unit time); thus it is the most commonly cited property of any radioisotope. For a given number of atoms, isotopes with shorter half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table 14.6, along with some of their applications.

Table 21.4.2: Half-Lives and Applications of Some Radioactive Isotopes

Radioactive Isotope	Half-Life	Typical Uses
hydrogen-3 (tritium)	12.32 yr	biochemical tracer
carbon-11	20.33 min	positron emission tomography (biomedical imaging)
carbon-14	5.70×10^3 yr	dating of artifacts
sodium-24	14.951 h	cardiovascular system tracer
phosphorus-32	14.26 days	biochemical tracer
potassium-40	1.248×10^9 yr	dating of rocks
iron-59	44.495 days	red blood cell lifetime tracer
cobalt-60	5.2712 yr	radiation therapy for cancer
technetium-99*m**	6.006 h	biomedical imaging
iodine-131	8.0207 days	thyroid studies tracer
radium-226	1.600×10^3 yr	radiation therapy for cancer
uranium-238	4.468×10^9 yr	dating of rocks and Earth's crust
americium-241	432.2 yr	smoke detectors
***The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.**		

Note

Radioactive decay is a first-order process.

Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as radioisotope dating techniques.

The most common method for measuring the age of ancient objects is carbon-14 dating. The carbon-14 isotope, created continuously in the upper regions of Earth's atmosphere, reacts with atmospheric oxygen or ozone to form $^{14}CO_2$. As a result, the CO_2 that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}CO_2$ molecules as well as nonradioactive $^{12}CO_2$ and $^{13}CO_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as beta decay, which releases low-energy electrons (β particles) that can be detected and measured:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + \beta^- \tag{21.4.9}$$

The half-life for this reaction is 5700 ± 30 yr.

The $^{14}C/^{12}C$ ratio in living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g of carbon (Figure 21.4.2). Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables scientists to estimate the age of the artifact, as illustrated in Example 11.Using this method implicitly assumes that the $^{14}CO_2/^{12}CO_2$ ratio in the atmosphere is constant, which is not strictly correct. Other methods, such as tree-ring dating, have been used to calibrate the dates obtained by radiocarbon dating, and all radiocarbon dates reported are now corrected for minor changes in the $^{14}CO_2/^{12}CO_2$ ratio over time.

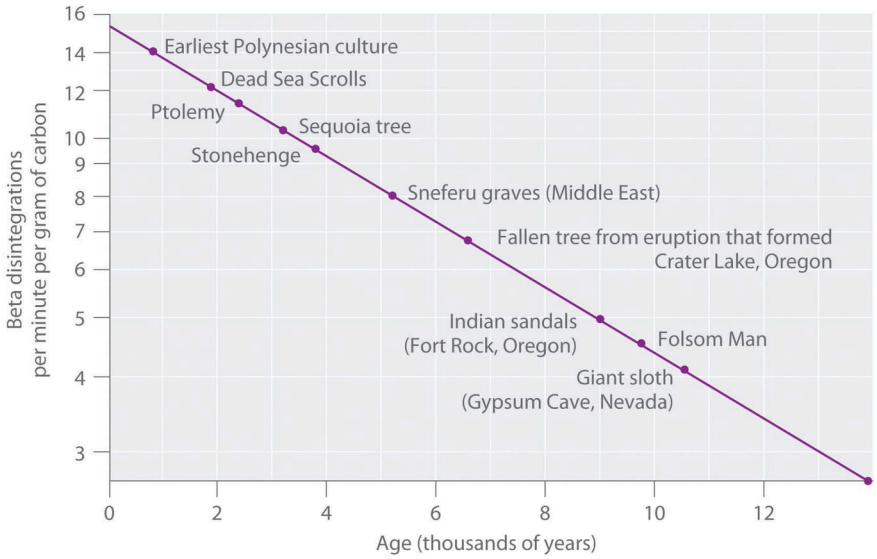


Figure 21.4.2: Radiocarbon Dating. A plot of the specific activity of ^{14}C versus age for a number of archaeological samples shows an inverse linear relationship between ^{14}C content (a log scale) and age (a linear scale).

Example 21.4.2

In 1990, the remains of an apparently prehistoric man were found in a melting glacier in the Italian Alps. Analysis of the ^{14}C content of samples of wood from his tools gave a decay rate of 8.0 dpm/g carbon. How long ago did the man die?

Given: isotope and final activity

Asked for: elapsed time

Strategy: Step A

Use Equation 21.4.5 to calculate N_0/N. Then substitute the value for the half-life of ^{14}C into Equation 21.4.3 to find the rate constant for the reaction.

Strategy: Step B

Using the values obtained for N_0/N and the rate constant, solve Equation 21.4.8 to obtain the elapsed time.

Solution

We know the initial activity from the isotope's identity (15 dpm/g), the final activity (8.0 dpm/g), and the half-life, so we can use the integrated rate law for a first-order nuclear reaction (Equation 21.4.8) to calculate the elapsed time (the amount of time elapsed since the wood for the tools was cut and began to decay).

$$\ln \frac{N}{N_0} = -kt \tag{21.4.10}$$

$$\frac{\ln(N_0/N)}{k} = t \tag{21.4.11}$$

Step A

From Equation 21.4.5, we know that $A = kN$. We can therefore use the initial and final activities (A_0 = 15 dpm and A = 8.0 dpm) to calculate N_0/N:

$$\frac{A_0}{A} = \frac{kN_0}{kN} = \frac{N_0}{N} = \frac{15}{8.0}$$

Now we need only calculate the rate constant for the reaction from its half-life (5730 yr) using Equation 21.4.3:

$$t_{1/2} = \frac{0.693}{k}$$

This equation can be rearranged as follows:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\ \text{yr}} = 1.22 \times 10^{-4}\ \text{yr}^{-1}$$

Step B

Substituting into the equation for t,

$$t = \frac{\ln(N_0/N)}{k} = \frac{\ln(15/8.0)}{1.22 \times 10^{-4}\ \text{yr}^{-1}} = 5.2 \times 10^{3}\ \text{yr}$$

From our calculations, the man died 5200 yr ago.

Exercise 21.4.2

It is believed that humans first arrived in the Western Hemisphere during the last Ice Age, presumably by traveling over an exposed land bridge between Siberia and Alaska. Archaeologists have estimated that this occurred about 11,000 yr ago, but some argue that recent discoveries in several sites in North and South America suggest a much earlier arrival. Analysis of a sample of charcoal from a fire in one such site gave a ^{14}C decay rate of 0.4 dpm/g of carbon. What is the approximate age of the sample?

Answer available at the end of this section.

Summary

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

The half-life of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction: $t_{1/2} = 0.693/k$. Radioactive decay reactions are first-order reactions. The rate of decay, or activity, of a sample of a radioactive substance is the decrease in the number of radioactive nuclei per unit time.

Answers

Exercise 21.4.1

4.3×10^5 s = 120 h = 5.0 days;

4.8×10^{-3} M

Exercise 21.4.2

30,000 yr

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21.5: Energy Changes in Nuclear Reactions

Learning Objectives

- To calculate a mass-energy balance and a nuclear binding energy.
- To understand the differences between nuclear fission and fusion.

Nuclear reactions, like chemical reactions, are accompanied by changes in energy. The energy changes in nuclear reactions, however, are enormous compared with those of even the most energetic chemical reactions. In fact, the energy changes in a typical nuclear reaction are so large that they result in a measurable change of mass. In this section, we describe the relationship between mass and energy in nuclear reactions and show how the seemingly small changes in mass that accompany nuclear reactions result in the release of enormous amounts of energy.

Mass–Energy Balance

The relationship between mass (m) and energy (E) is expressed in the following equation:

$$E = mc^2 \tag{21.5.1}$$

where

- c is the speed of light ($2.998 \times 10^8 \ \ m/s$), and
- E and m are expressed in units of joules and kilograms, respectively.

Albert Einstein first derived this relationship in 1905 as part of his special theory of relativity: the mass of a particle is directly proportional to its energy. Thus according to Equation 21.5.1, every mass has an associated energy, and similarly, any reaction that involves a change in energy must be accompanied by a change in mass. This implies that all exothermic reactions should be accompanied by a decrease in mass, and all endothermic reactions should be accompanied by an increase in mass. Given the law of conservation of mass, how can this be true? The solution to this apparent contradiction is that chemical reactions are indeed accompanied by changes in mass, but these changes are simply too small to be detected. As you may recall, all particles exhibit wavelike behavior, but the wavelength is inversely proportional to the mass of the particle (actually, to its momentum, the product of its mass and velocity). Consequently, wavelike behavior is detectable only for particles with very small masses, such as electrons. For example, the chemical equation for the combustion of graphite to produce carbon dioxide is as follows:

$$\mathrm{C(graphite)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta H^\circ = -393.5 \ \mathrm{kJ/mol} \tag{21.5.2}$$

Combustion reactions are typically carried out at constant pressure, and under these conditions, the heat released or absorbed is equal to ΔH. When a reaction is carried out at constant volume, the heat released or absorbed is equal to ΔE. For most chemical reactions, however, ΔE ≈ ΔH. If we rewrite Einstein's equation as

$$\Delta E = (\Delta m)c^2 \tag{21.5.3}$$

we can rearrange the equation to obtain the following relationship between the change in mass and the change in energy:

$$\Delta m = \frac{\Delta E}{c^2} \tag{21.5.4}$$

Because 1 J = 1 (kg•m^2)/s^2, the change in mass is as follows:

$$\Delta m = \frac{-393.5 \ \mathrm{kJ/mol}}{(2.998 \times 10^8 \ \mathrm{m/s})^2} = \frac{-3.935 \times 10^5 (\mathrm{kg \cdot m^2})/(\mathrm{s^2 \cdot mol})}{(2.998 \times 10^8 \ \mathrm{m/s})^2} = -4.38 \times 10^{-12} \ \mathrm{kg/mol} \tag{21.5.5}$$

This is a mass change of about 3.6 × 10^{-10} g/g carbon that is burned, or about 100-millionths of the mass of an electron per atom of carbon. In practice, this mass change is much too small to be measured experimentally and is negligible.

In contrast, for a typical nuclear reaction, such as the radioactive decay of ^{14}C to ^{14}N and an electron (a β particle), there is a much larger change in mass:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + {}^{0}_{-1}\beta \tag{21.5.6}$$

We can use the experimentally measured masses of subatomic particles and common isotopes given in Table 20.1 to calculate the change in mass directly. The reaction involves the conversion of a neutral ^{14}C atom to a positively charged ^{14}N ion (with six, not seven, electrons) and a negatively charged β particle (an electron), so the mass of the products is identical to the mass of a neutral ^{14}N atom. The total change in mass during the reaction is therefore the difference between the mass of a neutral ^{14}N atom (14.003074 amu) and the mass of a ^{14}C atom (14.003242 amu):

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} \tag{21.5.7}$$

$$= 14.003074 \text{ amu} - 14.003242 \text{ amu} = -0.000168 \text{ amu} \tag{21.5.8}$$

The difference in mass, which has been released as energy, corresponds to almost one-third of an electron. The change in mass for the decay of 1 mol of ^{14}C is –0.000168 g = $–1.68 \times 10^{-4}$ g = $–1.68 \times 10^{-7}$ kg. Although a mass change of this magnitude may seem small, it is about 1000 times larger than the mass change for the combustion of graphite. The energy change is as follows:

$$\Delta E = (\Delta m)c^2 = (-1.68 \times 10^{-7} \text{ kg})(2.998 \times 10^{8} \text{ m/s})^2 \tag{21.5.9}$$

$$= -1.51 \times 10^{10} (\text{kg} \cdot \text{m}^2)/\text{s}^2 = -1.51 \times 10^{10} \text{ J} = -1.51 \times 10^{7} \text{ kJ} \tag{21.5.10}$$

The energy released in this nuclear reaction is more than 100,000 times greater than that of a typical chemical reaction, even though the decay of ^{14}C is a relatively low-energy nuclear reaction.

Because the energy changes in nuclear reactions are so large, they are often expressed in kiloelectronvolts (1 keV = 10^3 eV), megaelectronvolts (1 MeV = 10^6 eV), and even gigaelectronvolts (1 GeV = 10^9 eV) per atom or particle. The change in energy that accompanies a nuclear reaction can be calculated from the change in mass using the relationship 1 amu = 931 MeV. The energy released by the decay of one atom of ^{14}C is thus

$$(-1.68 \times 10^{-4} \,\text{amu}) \left(\frac{931 \,\text{MeV}}{\text{amu}} \right) = -0.156 \,\text{MeV} = -156 \,\text{keV}$$

Example 21.5.1

Calculate the changes in mass (in atomic mass units) and energy (in joules per mole and electronvolts per atom) that accompany the radioactive decay of ^{238}U to ^{234}Th and an α particle. The α particle absorbs two electrons from the surrounding matter to form a helium atom.

Given: nuclear decay reaction

Asked for: changes in mass and energy

Strategy:

A Use the mass values in Table 20.1 to calculate the change in mass for the decay reaction in atomic mass units.

B Use Equation 21.5.4 to calculate the change in energy in joules per mole.

C Use the relationship between atomic mass units and megaelectronvolts to calculate the change in energy in electronvolts per atom.

Solution

A Using particle and isotope masses from Table 20.1, we can calculate the change in mass as follows:

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} = (\text{mass } {}^{234}\text{Th} + \text{mass } {}^{4}_{2}\text{He}) - \text{mass } {}^{238}\text{U} \tag{21.5.11}$$

$$= (234.043601 \text{ amu} + 4.002603 \text{ amu}) - 238.050788 \text{ amu} = -0.004584 \text{ amu} \tag{21.5.12}$$

B Thus the change in mass for 1 mol of ^{238}U is −0.004584 g or -4.584×10^{-6} kg. The change in energy in joules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-4.584 \times 10^{-6}\ \text{kg})(2.998 \times 10^{8}\ \text{m/s})^2 = -4.120 \times 10^{11}\ \text{J/mol}$$

C The change in energy in electronvolts per atom is as follows:

$$\Delta E = -4.584 \times 10^{-3}\ \text{amu} \times \frac{931\ \text{MeV}}{\text{amu}} \times \frac{1 \times 10^{6}\ \text{eV}}{1\ \text{MeV}} = -4.27 \times 10^{6}\ \text{eV/atom}$$

Exercise 21.5.1

Calculate the changes in mass (in atomic mass units) and energy (in kilojoules per mole and kiloelectronvolts per atom) that accompany the radioactive decay of tritium (^{3}H) to ^{3}He and a β particle.

Answer available at the end of this section.

Nuclear Binding Energies

We have seen that energy changes in both chemical and nuclear reactions are accompanied by changes in mass. Einstein's equation, which allows us to interconvert mass and energy, has another interesting consequence: The mass of an atom is always less than the sum of the masses of its component particles. The only exception to this rule is hydrogen-1 (^{1}H), whose measured mass of 1.007825 amu is identical to the sum of the masses of a proton and an electron. In contrast, the experimentally measured mass of an atom of deuterium (^{2}H) is 2.014102 amu, although its calculated mass is 2.016490 amu:

$$m_{^2\text{H}} = m_{\text{neutron}} + m_{\text{proton}} + m_{\text{electron}} \tag{21.5.13}$$

$$= 1.008665\ \text{amu} + 1.007276\ \text{amu} + 0.000549\ \text{amu} = 2.016490\ \text{amu} \tag{21.5.14}$$

The difference between the sum of the masses of the components and the measured atomic mass is called the **mass defect** of the nucleus. Just as a molecule is more stable than its isolated atoms, a nucleus is more stable (lower in energy) than its isolated components. Consequently, when isolated nucleons assemble into a stable nucleus, energy is released. According to Equation 21.5.4, this release of energy must be accompanied by a decrease in the mass of the nucleus.

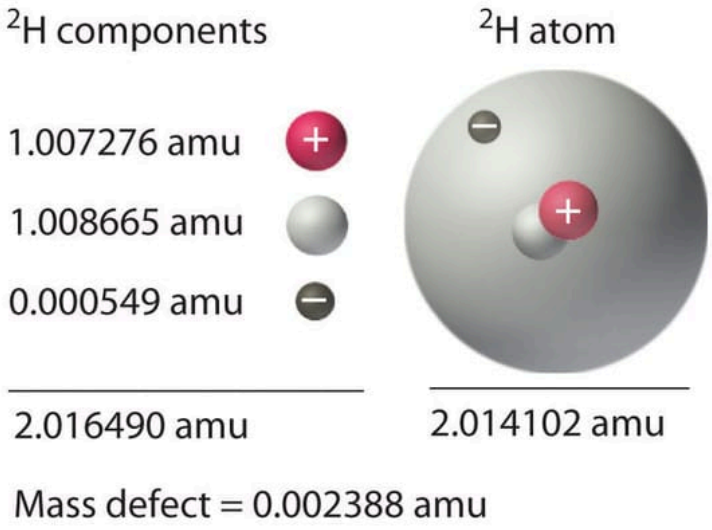


Figure 21.5.1: Nuclear Binding Energy in Deuterium. The mass of a ^{2}H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the mass defect, the greater the nuclear binding energy and the more stable the nucleus.

The amount of energy released when a nucleus forms from its component nucleons is the **nuclear binding energy** (Figure 21.5.1). In the case of deuterium, the mass defect is 0.002388 amu, which corresponds to a nuclear binding energy of 2.22 MeV for the deuterium nucleus. Because the magnitude of the mass defect is proportional to the nuclear binding energy, both values indicate the stability of the nucleus.

> Just as a molecule is more stable (lower in energy) than its isolated atoms, a nucleus is more stable than its isolated components.

Not all nuclei are equally stable. Chemists describe the relative stability of different nuclei by comparing the binding energy per nucleon, which is obtained by dividing the nuclear binding energy by the mass number (A) of the nucleus. As shown in Figure 21.5.2, the binding energy per nucleon increases rapidly with increasing atomic number until about Z = 26, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., ^{4}He, ^{12}C, and ^{16}O). As mentioned earlier, these are particularly stable combinations.

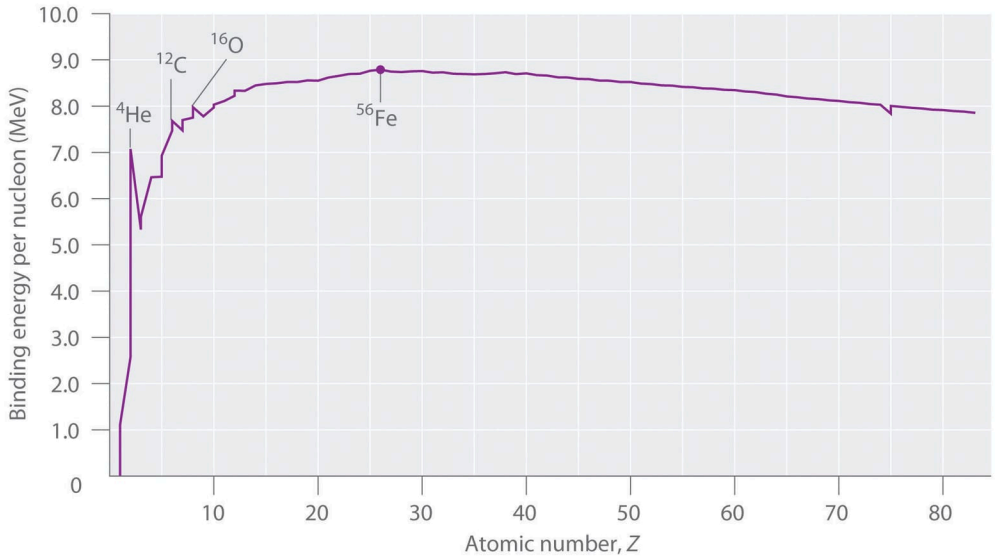


Figure 21.5.2: The Curve of Nuclear Binding Energy. This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.

Because the maximum binding energy per nucleon is reached at ^{56}Fe, all other nuclei are thermodynamically unstable with regard to the formation of ^{56}Fe. Consequently, heavier nuclei (toward the right in Figure 21.5.2) should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 21.5.2) should spontaneously undergo reactions that result in an increase in atomic number. This is indeed the observed pattern.

> Heavier nuclei spontaneously undergo nuclear reactions that *decrease* their atomic number. Lighter nuclei spontaneously undergo nuclear reactions that *increase* their atomic number.

Example 21.5.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{56}Fe. The experimental mass of the nuclide is given in Table A4.

Given: nuclide and mass

Asked for: nuclear binding energy and binding energy per nucleon

Strategy:

A Sum the masses of the protons, electrons, and neutrons or, alternatively, use the mass of the appropriate number of ^{1}H atoms (because its mass is the same as the mass of one electron and one proton).

B Calculate the mass defect by subtracting the experimental mass from the calculated mass.

C Determine the nuclear binding energy by multiplying the mass defect by the change in energy in electronvolts per atom. Divide this value by the number of nucleons to obtain the binding energy per nucleon.

Solution

A An iron-56 atom has 26 protons, 26 electrons, and 30 neutrons. We could add the masses of these three sets of particles; however, noting that 26 protons and 26 electrons are equivalent to 26 ^{1}H atoms, we can calculate the sum of the masses more quickly as follows:

$$\begin{aligned} \text{calculated mass} &= 26(\text{mass } {}^{1}_{1}\text{H}) + 30(\text{mass } {}^{1}_{0}\text{n}) \\ &= 26(1.007825)\text{amu} + 30(1.008665)\text{amu} = 56.463400 \text{ amu} \\ \text{experimental mass} &= 55.934938 \end{aligned}$$

B We subtract to find the mass defect:

$$\begin{aligned} \text{mass defect} &= \text{calculated mass} - \text{experimental mass} \\ &= 56.463400 \text{ amu} - 55.934938 \text{ amu} = 0.528462 \text{ amu} \end{aligned}$$

C The nuclear binding energy is thus 0.528462 amu × 931 MeV/amu = 492 MeV. The binding energy per nucleon is 492 MeV/56 nucleons = 8.79 MeV/nucleon.

Exercise 21.5.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{238}U.

Answer available at the end of this section.

Summary

Unlike a chemical reaction, a nuclear reaction results in a significant change in mass and an associated change of energy, as described by Einstein's equation. Nuclear reactions are accompanied by large changes in energy, which result in detectable changes in mass. The change in mass is related to the change in energy according to Einstein's equation: $\Delta E = (\Delta m)c^2$. Large changes in energy are usually reported in kiloelectronvolts or megaelectronvolts (thousands or millions of electronvolts). With the exception of ^{1}H, the experimentally determined mass of an atom is always less than the sum of the masses of the component particles (protons, neutrons, and electrons) by an amount called the mass defect of the nucleus. The energy corresponding to the mass defect is the nuclear binding energy, the amount of energy released when a nucleus forms from its component particles. In nuclear fission, nuclei split into lighter nuclei with an accompanying release of multiple neutrons and large amounts of energy. The critical mass is the minimum mass required to support a self-sustaining nuclear chain reaction. Nuclear fusion is a process in which two light nuclei combine to produce a heavier nucleus plus a great deal of energy.

Answers

Exercise 21.5.1

$\Delta m = -2.0 \times 10^{-5}$ amu; $\Delta E = -1.9 \times 10^{6}$ kJ/mol = −19 keV/atom

Exercise 21.5.2

1800 MeV/^{238}U; 7.57 MeV/nucleon

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21.6: Nuclear Fission

Learning Objectives

- Explain nuclear fission
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56. Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 21.6.1.

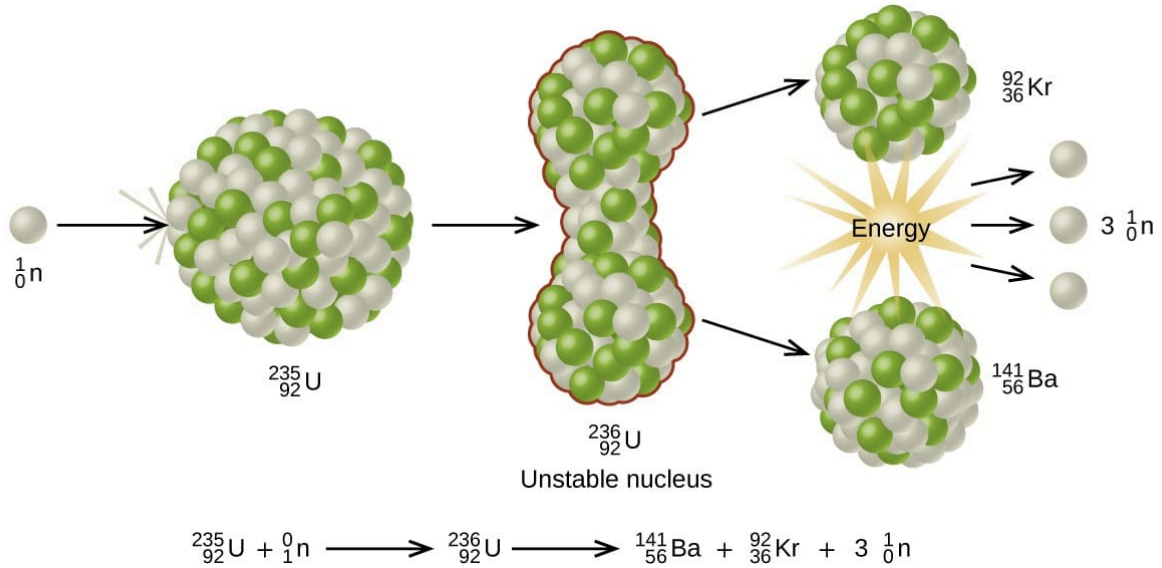


Figure 21.6.1: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure 21.6.2. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{90}_{38}Sr + {}^{144}_{54}Xe + 2\ {}^{1}_{0}n$$

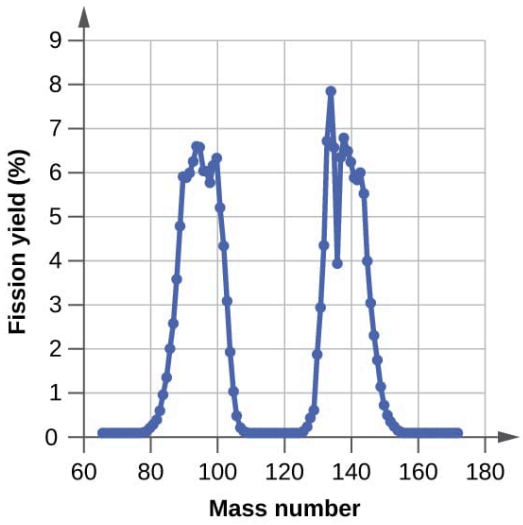
$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{87}_{35}Br + {}^{146}_{57}La + 3\ {}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{96}_{37}Rb + {}^{137}_{55}Cs + 3\ {}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{137}_{52}Te + {}^{97}_{40}Zr + 2\ {}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\ {}^{1}_{0}n$$

(a)



(b)

Figure 21.6.2: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure 21.6.3). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

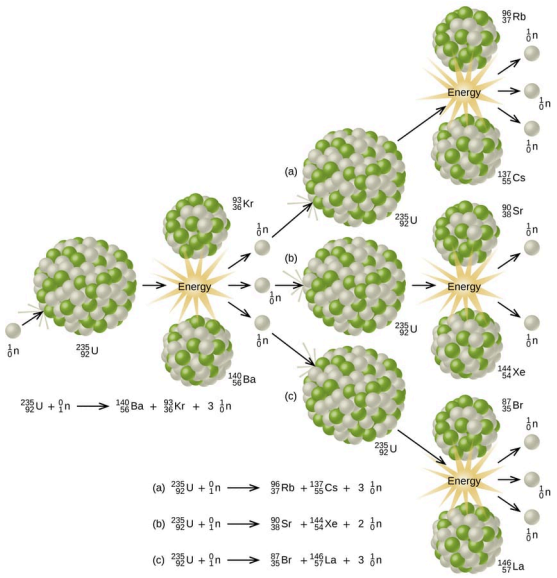


Figure 21.6.3: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-

sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure 21.6.4).

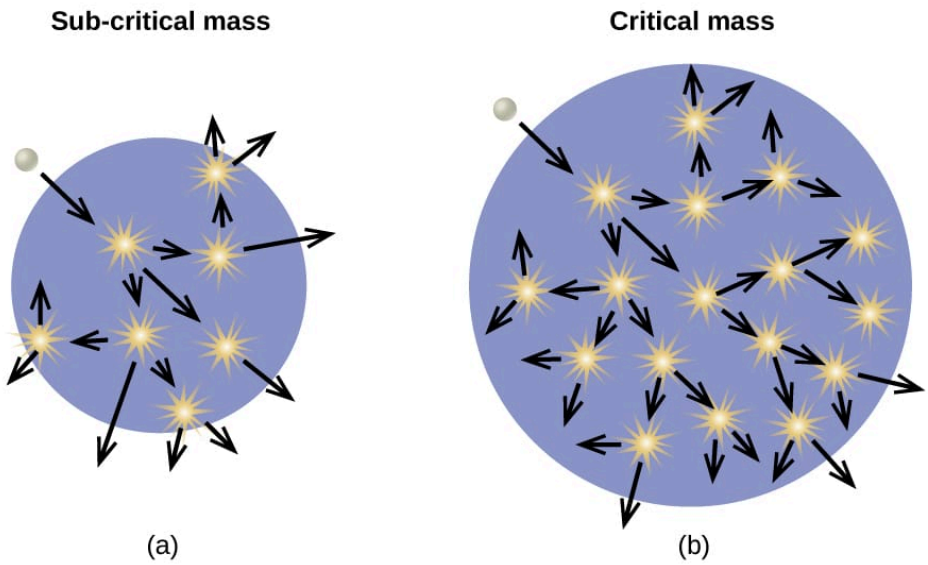


Figure 21.6.4: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (Figure 21.6.5) contains several pounds of fissionable material, $^{235}_{92}\mathrm{U}$ or $^{239}_{94}\mathrm{Pu}$, a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

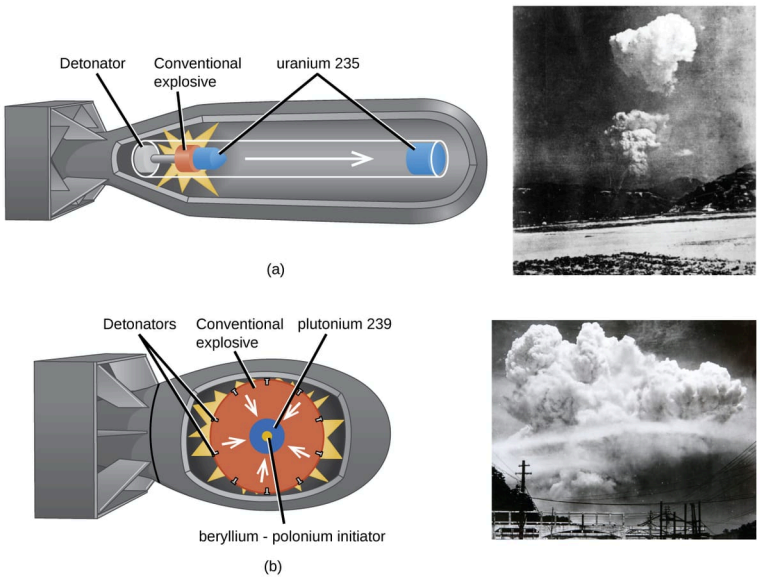


Figure 21.6.5: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 12, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a nuclear reactor (Figure 21.6.6). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

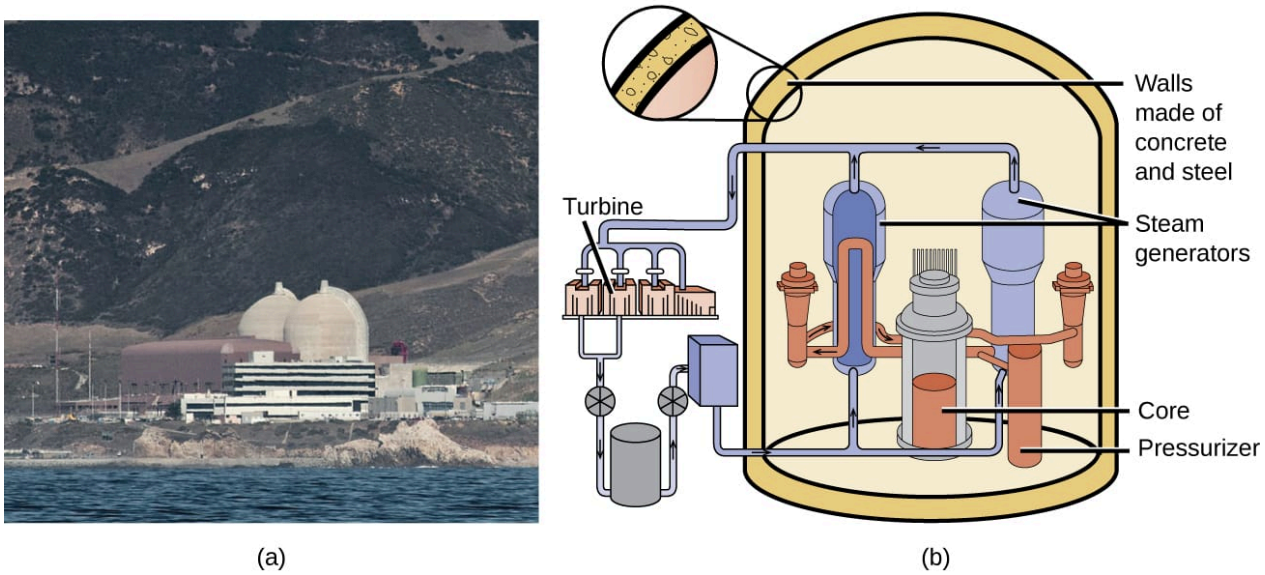


Figure 21.6.6: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by “Mike” Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham’s law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (Figure 21.6.4). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A nuclear moderator is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water (${}^{2}_{1}\mathrm{H_2O}$) or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use control rods (Figure 21.6.8) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$ {}^{10}_{5}\mathrm{B} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He} \tag{21.6.1} $$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

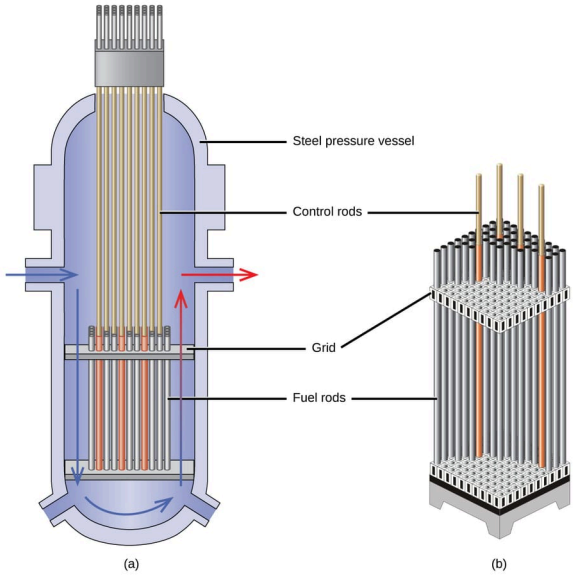


Figure 21.6.7: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, glossar.periodni.com/glossar...en=control+rod)

Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating

personnel from the radiation. Reactors are equipped with a containment system (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video $21.6.1$***:*** *Click here to watch a 3-minute video from the Nuclear Energy Institute on how nuclear reactors work.*

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g) \tag{21.6.2}$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure $21.6.8$).

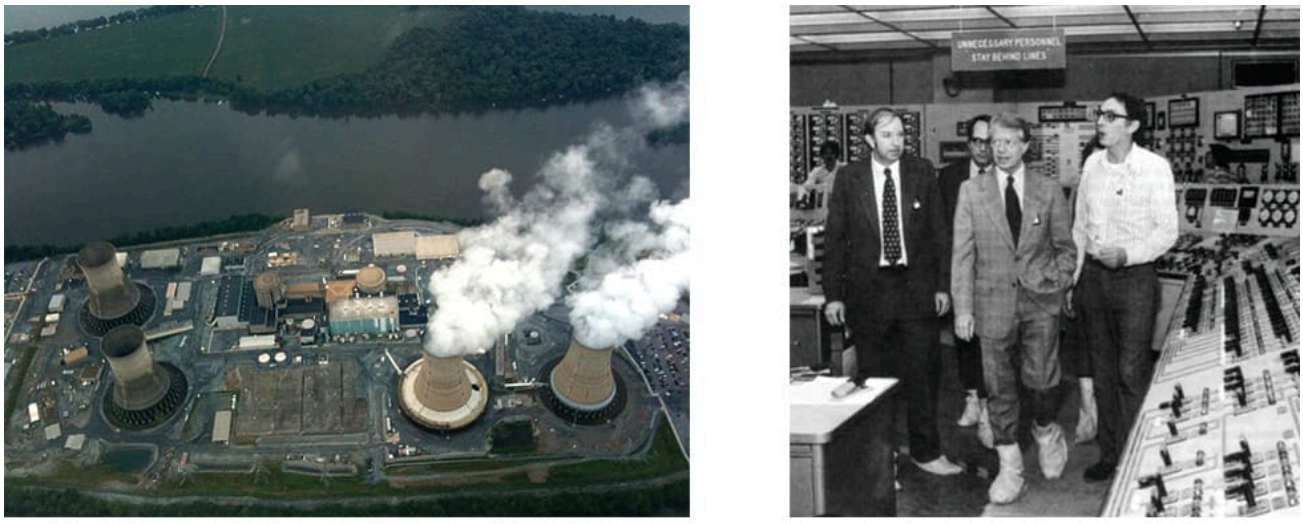


Figure 21.6.8: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 21.6.10).



Figure 21.6.9: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Contributors and Attributions

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21.7: Nuclear Fusion

Learning Objectives

- Describe the nuclear reactions in a nuclear fusion reaction
- Quantify the energy released or absorbed in a fusion reaction

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{n} \tag{21.7.1}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}^{4}_{2}\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}^{2}_{1}H$ and a triton, ${}^{3}_{1}H$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n} \tag{21.7.2}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^{9} kilojoules per mole of ${}^{4}_{2}\mathrm{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

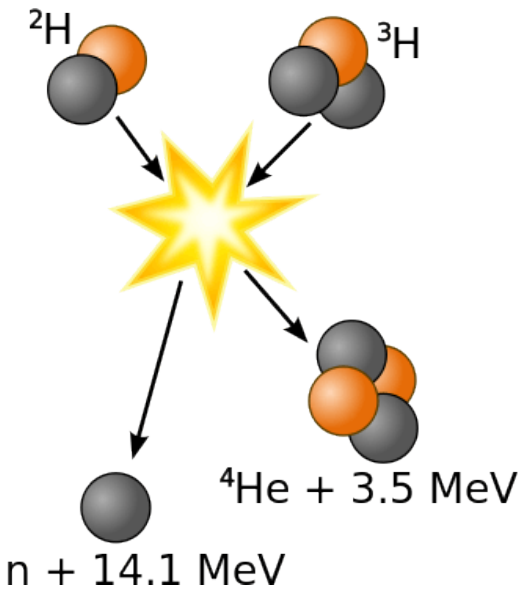


Figure 21.7.1: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of particles.[Image use with permission via Wikipedia (Wykis)

The most important fusion process in nature is the one that powers stars. In the 20th century, it was realized that the energy released from nuclear fusion reactions accounted for the longevity of the Sun and other stars as a source of heat and light. The fusion of nuclei in a star, starting from its initial hydrogen and helium abundance, provides that energy and synthesizes new nuclei as a byproduct of that fusion process. The prime energy producer in the Sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the

release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure 21.7.2).

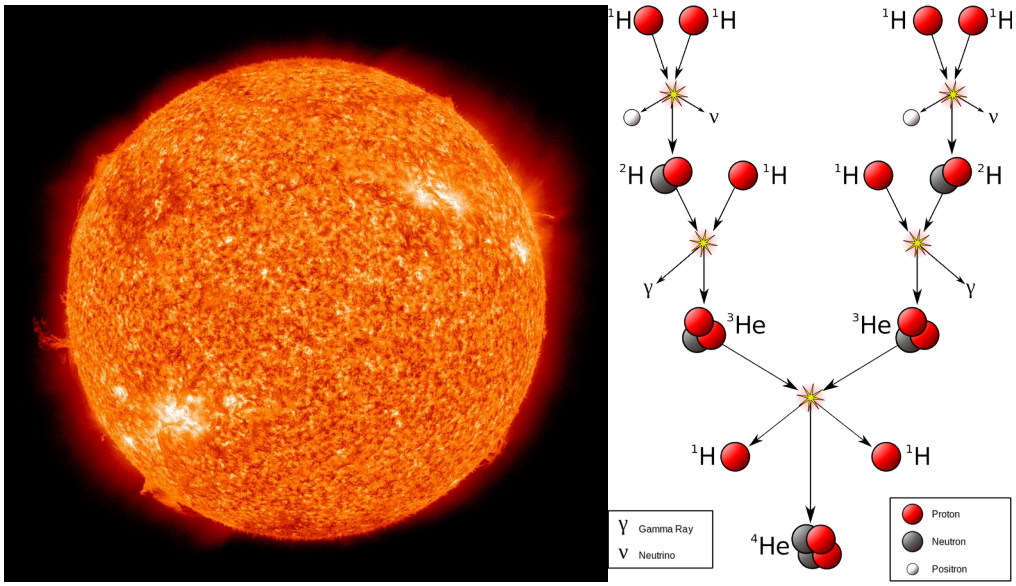


Figure 21.7.2: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

Example 21.7.1

Calculate the energy released in each of the following hypothetical processes.

a. $3\,{}^{4}_{2}\mathrm{He} \rightarrow {}^{12}_{6}\mathrm{C}$
b. $6\,{}^{1}_{1}\mathrm{H} + 6\,{}^{1}_{0}\mathrm{n} \rightarrow {}^{12}_{6}\mathrm{C}$
c. $6\,{}^{2}_{1}\mathrm{D} \rightarrow {}^{12}_{6}\mathrm{C}$

Solution

a. $Q_a = 3 \times 4.0026 - 12.000)\ amu \times (1.4924 \times 10^{-10}\ J/amu) = 1.17 \times 10^{-12}\ J$
b. $Q_b = (6 \times (1.007825 + 1.008665) - 12.00000)\ amu \times (1.4924 \times 10^{1-0} J/amu) = 1.476 \times 10^{-11}\ J$
c. $Q_c = 6 \times 2.014102 - 12.00000\ amu \times (1.4924 \times 10^{-10}\ J/amu) = 1.263 \times 10^{-11}\ J$

Fusion of He to give C releases the least amount of energy, because the fusion to produce He has released a large amount. The difference between the second and the third is the binding energy of deuterium. The conservation of mass-and-energy is well illustrated in these calculations. On the other hand, the calculation is based on the conservation of mass-and-energy.

Nuclear Reactors

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

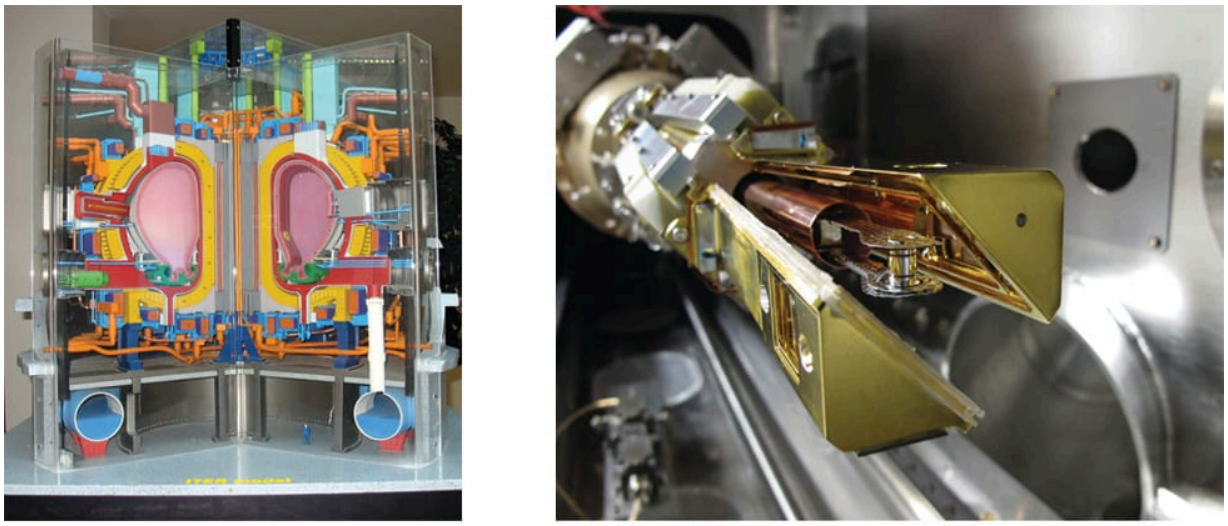


Figure 21.7.3: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving larg\times 10^{scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 21.7.3). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.Contributors

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21.8: Biological Effects of Radiation

Learning Objectives

- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle is an ionized helium nucleus (He^{2+}) that can act as a powerful oxidant. In this section, we describe how radiation interacts with matter and the some of the chemical and biological effects of radiation.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. **Nonionizing radiation** is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, **ionizing radiation** is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$\text{atom} + \text{ionizing radiation} \rightarrow \text{ion}^+ + \text{e}^- \tag{21.8.1}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 21.8.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle:

$$1 \text{ MeV/particle} = 96 \text{ billion J/mol}.$$



Figure 21.8.1: Radiation Damage. When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue. (CC BY-SA-NC; anonymous)

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

The relative abilities of the various forms of ionizing radiation to penetrate biological tissues are illustrated in Figure 21.8.2. Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

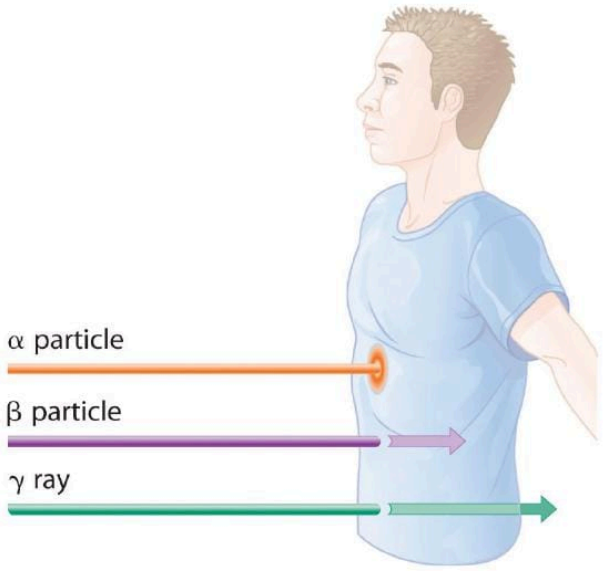


Figure 21.8.2: Depth of Penetration of Ionizing Radiation. The depth of penetration of alpha, beta, and gamma radiation varies with the particle. Because α particles interact strongly with matter, they do not penetrate deeply into the human body. In contrast, β particles do not interact as strongly with matter and penetrate more deeply. Gamma rays, which have no charge, are stopped by only very dense materials and can pass right through the human body without being absorbed. (CC BY-SA-NC; anonymous)

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 21.8.1.

Table 21.8.1: Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
x-rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2}–10^{1}	< 20 cm	> 3 m
***Distance at which half of the radiation has been absorbed.**			

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air. The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1 \text{ rad} = 0.010 \text{ J/kg} \qquad 1 \text{ Gy} = 1 \text{ J/kg} \tag{21.8.2}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the **rem (roentgen equivalent in man)** was devised to describe the actual amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the RBE (relative biological effectiveness) factor, which is 1 for β particles, γ rays, and x-rays and about 20 for α particles. Because actual radiation doses tend to be very small, most measurements are reported in millirems (1 mrem = 10^{-3} rem).

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

Natural Sources of Radiation

We are continuously exposed to measurable background radiation from a variety of natural sources, which, on average, is equal to about 150–600 mrem/yr (Figure 21.8.3). One component of background radiation is *cosmic rays*, high-energy particles and γ rays emitted by the sun and other stars, which bombard Earth continuously. Because cosmic rays are partially absorbed by the atmosphere before they reach Earth's surface, the exposure of people living at sea level (about 30 mrem/yr) is significantly less than the exposure of people living at higher altitudes (about 50 mrem/yr in Denver, Colorado). Every 4 hours spent in an airplane at greater than 30,000 ft adds about 1 mrem to a person's annual radiation exposure.

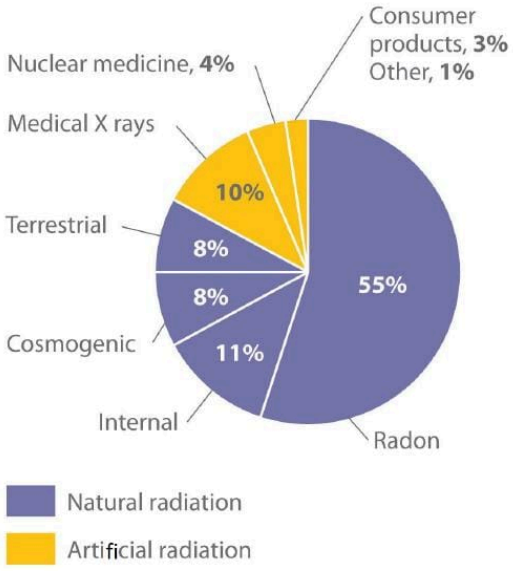


Figure 21.8.3: The Radiation Exposure of a Typical Adult in the United States. The average radiation dose from natural sources for an adult in the United States is about 150–600 mrem/yr. Radon accounts for more than half of an adult's total radiation exposure, whereas background radiation (terrestrial and cosmogenic) and exposure from medical sources account for about 15% each. Data source: Office of Civilian Radioactive Waste Management (CC BY-SA-NC; anonymous)

A second component of background radiation is *cosmogenic radiation*, produced by the interaction of cosmic rays with gases in the upper atmosphere. When high-energy cosmic rays collide with oxygen and nitrogen atoms, neutrons and protons are released. These, in turn, react with other atoms to produce radioactive isotopes, such as ^{14}C:

$$^{14}_{7}\mathrm{N} + {}_{0}{}^{1}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{21.8.3}$$

The carbon atoms react with oxygen atoms to form CO_2, which is eventually washed to Earth's surface in rain and taken up by

plants. About 1 atom in 1×10^{12} of the carbon atoms in our bodies is radioactive ^{14}C, which decays by beta emission. About 5000 ^{14}C nuclei disintegrate in your body during the 15 s or so that it takes you to read this paragraph. Tritium (^{3}H) is also produced in the upper atmosphere and falls to Earth in precipitation. The total radiation dose attributable to ^{14}C is estimated to be 1 mrem/yr, while that due to ^{3}H is about 1000 times less.

The third major component of background radiation is *terrestrial radiation*, which is due to the remnants of radioactive elements that were present on primordial Earth and their decay products. For example, many rocks and minerals in the soil contain small amounts of radioactive isotopes, such as $^{232}\mathrm{Th}$ and $^{238}\mathrm{U}$ as well as radioactive daughter isotopes, such as $^{226}\mathrm{Ra}$. The amount of background radiation from these sources is about the same as that from cosmic rays (approximately 30 mrem/yr). These isotopes are also found in small amounts in building materials derived from rocks and minerals, which significantly increases the radiation exposure for people who live in brick or concrete-block houses (60–160 mrem/yr) instead of houses made of wood (10–20 mrem/yr). Our tissues also absorb radiation (about 40 mrem/yr) from naturally occurring radioactive elements that are present in our bodies. For example, the average adult contains about 140 g of potassium as the K^+ ion. Naturally occurring potassium contains 0.0117% $^{40}\mathrm{K}$, which decays by emitting both a β particle and a (\gamma\) ray. In the last 20 seconds, about the time it took you to read this paragraph, approximately 40,000 $^{40}\mathrm{K}$ nuclei disintegrated in your body.

By far the most important source of background radiation is radon, the heaviest of the noble gases (group 18). Radon-222 is produced during the decay of ^{238}U, and other isotopes of radon are produced by the decay of other heavy elements. Even though radon is chemically inert, all its isotopes are radioactive. For example, ^{222}Rn undergoes two successive alpha-decay events to give ^{214}Pb:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\alpha^{+} + {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\alpha^{+} + {}^{214}_{82}\mathrm{Pb} \tag{21.8.4}$$

Because radon is a dense gas, it tends to accumulate in enclosed spaces such as basements, especially in locations where the soil contains greater-than-average amounts of naturally occurring uranium minerals. Under most conditions, radioactive decay of radon poses no problems because of the very short range of the emitted α particle. If an atom of radon happens to be in your lungs when it decays, however, the chemically reactive daughter isotope polonium-218 can become irreversibly bound to molecules in the lung tissue. Subsequent decay of $^{218}\mathrm{Po}$ releases an α particle directly into one of the cells lining the lung, and the resulting damage can eventually cause lung cancer. The $^{218}\mathrm{Po}$ isotope is also readily absorbed by particles in cigarette smoke, which adhere to the surface of the lungs and can hold the radioactive isotope in place. Recent estimates suggest that radon exposure is a contributing factor in about 15% of the deaths due to lung cancer. Because of the potential health problem radon poses, many states require houses to be tested for radon before they can be sold. By current estimates, radon accounts for more than half of the radiation exposure of a typical adult in the United States.

Artificial Sources of Radiation

In addition to naturally occurring background radiation, humans are exposed to small amounts of radiation from a variety of artificial sources. The most important of these are the x-rays used for diagnostic purposes in medicine and dentistry, which are photons with much lower energy than γ rays. A single chest x-ray provides a radiation dose of about 10 mrem, and a dental x-ray about 2–3 mrem. Other minor sources include television screens and computer monitors with cathode-ray tubes, which also produce x-rays. Luminescent paints for watch dials originally used radium, a highly toxic alpha emitter if ingested by those painting the dials. Radium was replaced by tritium (^{3}H) and promethium (^{147}Pr), which emit low-energy β particles that are absorbed by the watch crystal or the glass covering the instrument. Radiation exposure from television screens, monitors, and luminescent dials totals about 2 mrem/yr. Residual fallout from previous atmospheric nuclear-weapons testing is estimated to account for about twice this amount, and the nuclear power industry accounts for less than 1 mrem/yr (about the same as a single 4 h jet flight).

Example 21.8.1

Calculate the annual radiation dose in rads a typical 70 kg chemistry student receives from the naturally occurring ^{40}K in his or her body, which contains about 140 g of potassium (as the K^+ ion). The natural abundance of ^{40}K is 0.0117%. Each 1.00 mol of ^{40}K undergoes 1.05×10^{7} decays/s, and each decay event is accompanied by the emission of a 1.32 MeV β particle.

Given: mass of student, mass of isotope, natural abundance, rate of decay, and energy of particle

Asked for: annual radiation dose in rads

Strategy:

A. Calculate the number of moles of ^{40}K present using its mass, molar mass, and natural abundance.
B. Determine the number of decays per year for this amount of ^{40}K.
C. Multiply the number of decays per year by the energy associated with each decay event. To obtain the annual radiation dose, use the mass of the student to convert this value to rads.

Solution

A The number of moles of ^{40}K present in the body is the total number of potassium atoms times the natural abundance of potassium atoms present as ^{40}K divided by the atomic mass of ^{40}K:

$$\text{moles } ^{40}\text{K} = 140 \text{ g K} \times \frac{0.0117 \text{ mol } ^{40}\text{K}}{100 \text{ mol K}} \times \frac{1 \text{ mol K}}{40.0 \text{ g K}} = 4.10 \times 10^{-4} \text{ mol } ^{40}\text{K}$$

B We are given the number of atoms of ^{40}K that decay per second in 1.00 mol of ^{40}K, so the number of decays per year is as follows:

$$\frac{\text{decays}}{\text{year}} = 4.10 \times 10^{-4} \text{ mol}^{40} \text{ K} \times \frac{1.05 \times 10^{7} \text{ decays/s}}{1.00 \text{ mol } ^{40}\text{K}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{365 \text{ days}}{1 \text{ yr}}$$

C The total energy the body receives per year from the decay of ^{40}K is equal to the total number of decays per year multiplied by the energy associated with each decay event:

$$\begin{aligned} \text{total energy per year} &= \frac{1.36 \times 10^{11} \text{ decays}}{\text{yr}} \times \frac{1.32 \text{ MeV}}{\text{decays}} \times \frac{10^{6} \text{ eV}}{\text{MeV}} \times \frac{1.602 \times 10^{-19} \text{ J}}{\text{eV}} \\ &= 2.87 \times 10^{-2} \text{ J/yr} \end{aligned}$$

We use the definition of the rad (1 rad = 10^{-2} J/kg of tissue) to convert this figure to a radiation dose in rads. If we assume the dose is equally distributed throughout the body, then the radiation dose per year is as follows:

$$\begin{aligned} \text{radiation dose per year} &= \frac{2.87 \times 10^{-2} \text{ J/yr}}{70.0 \text{ kg}} \times \frac{1 \text{ rad}}{1 \times 10^{-2} \text{ J/kg}} \\ &= 4.10 \times 10^{-2} \text{ rad/yr} = 41 \text{ mrad/yr} \end{aligned}$$

This corresponds to almost half of the normal background radiation most people experience.

Exercise 21.8.1

Because strontium is chemically similar to calcium, small amounts of the Sr^{2+} ion are taken up by the body and deposited in calcium-rich tissues such as bone, using the same mechanism that is responsible for the absorption of Ca^{2+}. Consequently, the radioactive strontium (^{90}Sr) found in fission waste and released by atmospheric nuclear-weapons testing is a major health concern. A normal 70 kg human body has about 280 mg of strontium, and each mole of ^{90}Sr undergoes 4.55×10^{14} decays/s by the emission of a 0.546 MeV β particle. What would be the annual radiation dose in rads for a 70 kg person if 0.10% of the strontium ingested were ^{90}Sr?

Answer available at the end of this section.

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 21.8.2. Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table 21.8.2: The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Both patterns are plotted in Figure 21.8.4, but which of the two is applicable to humans? According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that all exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

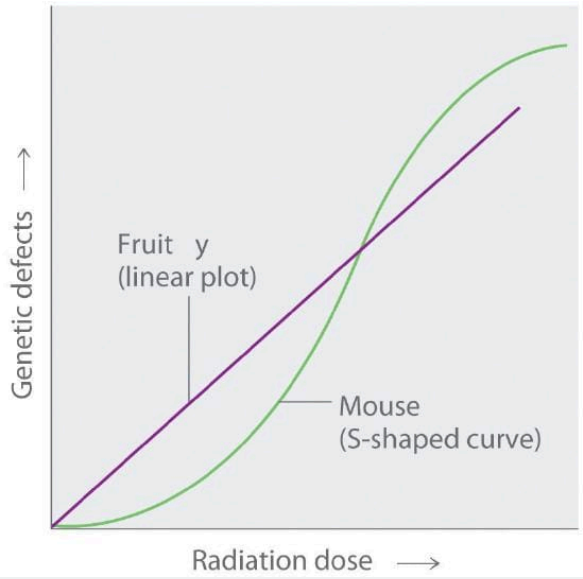


Figure 21.8.4: Two Possible Relationships between the Number of Genetic Defects and Radiation Exposure. Studies on fruit flies show a linear relationship between the number of genetic defects and the magnitude of the radiation dose and exposure time, which is consistent with a cumulative effect of radiation. In contrast, studies on mice show an S-shaped curve, which suggests that the number of defects is lower when radiation exposure occurs over a longer time. Which of these relationships is more applicable to humans is a matter of considerable debate. (CC BY-SA-NC; anonymous)

Graph of genetic defects against radiation dose. Fruit is graphed in purple and has a linear plot. Mouse is graphed in green and has a S shaped curve.

Summary

Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive. The effects of radiation on matter depend on the energy of the radiation. Nonionizing radiation is relatively low in energy, and the energy is transferred to matter in the form of heat. Ionizing radiation is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the roentgen (R), the amount of energy absorbed by dry air, and the rad (radiation absorbed dose), the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The rem (roentgen equivalent in man) measures the actual amount of tissue damage caused by a given amount of radiation. Natural sources of radiation include cosmic radiation, consisting of high-energy particles and γ rays emitted by the sun and other stars; cosmogenic radiation, which is produced by the interaction of cosmic rays with gases in the upper atmosphere; and terrestrial radiation, from radioactive elements present on primordial Earth and their decay products. The risks of ionizing radiation depend on the intensity of the radiation, the mode of exposure, and the duration of the exposure.

Answers

Exercise 21.8.1

5.7×10^3 rad/yr (which is 10 times the fatal dose)

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21.E: Exercises

21.1: Radioactivity

Q21.1.1

Why are many radioactive substances warm to the touch? Why do many radioactive substances glow?

Q21.1.2

Describe the differences between nonionizing and ionizing radiation in terms of the intensity of energy emitted and the effect each has on an atom or molecule after collision. Which nuclear decay reactions are more likely to produce ionizing radiation? nonionizing radiation?

Q21.1.3

Would you expect nonionizing or ionizing radiation to be more effective at treating cancer? Why?

S21.1.3

Ionizing radiation is higher in energy and causes greater tissue damage, so it is more likely to destroy cancerous cells.

Q21.1.4

Historically, concrete shelters have been used to protect people from nuclear blasts. Comment on the effectiveness of such shelters.

Q21.1.5

Gamma rays are a very high-energy radiation, yet α particles inflict more damage on biological tissue. Why?

Q21.1.6

List the three primary sources of naturally occurring radiation. Explain the factors that influence the dose that one receives throughout the year. Which is the largest contributor to overall exposure? Which is the most hazardous?

S21.1.6

Three primary naturally occurring radiations are radium, uranium and thorium, each all having long half lives. Inhalation of air, ingestion of food and water,terrestrial radation from the ground and cosmic radiation from space are all factors tat influence the does that a person receives throughout the year. Inhalation of the air is the largest contributor to exposure. Radiation can damage DNA or kill cells. When radiation is exposed to your body, it will collide with atoms and this will change and damage your DNA.

Q21.1.7

Because radon is a noble gas, it is inert and generally unreactive. Despite this, exposure to even low concentrations of radon in air is quite dangerous. Describe the physical consequences of exposure to radon gas. Why are people who smoke more susceptible to these effects?

Q21.1.8

Most medical imaging uses isotopes that have extremely short half-lives. These isotopes usually undergo only one kind of nuclear decay reaction. Which kind of decay reaction is usually used? Why? Why would a short half-life be preferred in these cases?

Beta decay. Alfa decay can be easily stopped by paper, which means it can not be used to see inside people's body. Also, Gamma rays are really dangerous for human, that even a short period of time exploding to it will have negative effect on human body. Thus, Beta decay is the perfect choice. It can be used to see through human's body and stopped by aluminum or some other metals.

Since all these radioactive decays are harmful for human body, if the half time of these reactions are short, the time exploding to these reactions will be short too.

Q21.1.9

Which would you prefer: one exposure of 100 rem, or 10 exposures of 10 rem each? Explain your rationale.

S21.1.9

Ten exposures of 10 rem are less likely to cause major damage.

Q21.1.10

A 2.14 kg sample of rock contains 0.0985 g of uranium. How much energy is emitted over 25 yr if 99.27% of the uranium is ^{238}U, which has a half-life of 4.46×10^9 yr, if each decay event is accompanied by the release of 4.039 MeV? If a 180 lb individual absorbs all of the emitted radiation, how much radiation has been absorbed in rads?

Q21.1.11

There is a story about a “radioactive boy scout” who attempted to convert thorium-232, which he isolated from about 1000 gas lantern mantles, to uranium-233 by bombarding the thorium with neutrons. The neutrons were generated via bombarding an aluminum target with α particles from the decay of americium-241, which was isolated from 100 smoke detectors. Write balanced nuclear reactions for these processes. The “radioactive boy scout” spent approximately 2 h/day with his experiment for 2 yr. Assuming that the alpha emission of americium has an energy of 5.24 MeV/particle and that the americium-241 was undergoing 3.5×10^6 decays/s, what was the exposure of the 60.0 kg scout in rads? The intrepid scientist apparently showed no ill effects from this exposure. Why?

241/95 Am---> 4/2 He + 237/93Np---> 4/2He + 233/91Pa----> 1/0n+ 232/91Th---> 1/1 H + 233/92 U

By adding alpha particles to the products side of the reaction, he was able to reduce the mass number by 4 and the atomic number by 2 to get the products he wanted. Bombardment with neutrons and 1 H was required to lower to the mass number to get Th and then raise both the mass number and the atomic number to yield Uranium.

2 hours*365*2= 1460 hours of exposure.*60min/1hr*60s/1min= 5.26*10^6s of exposure

1MeV= (1.6022*10^-13 Joules) * (5.24 MeV/particle)*2 particles= 1.679*10^-12 Joules.

(1.679*10^-12 Joules) * (1 amu/ 1.4924*10^-10 Joules)= 2.51*10^-13 amu

E=mc^2

E=(2.51*10^-13 amu)(1.66*10^-22kg/amu)(2.9998*10^8m/s)^2= (3.75*10^-18 kgm^2/s)*(3.5*10^6 decays/s)= 1.31*10^-11 joules of exposure per second.

The scientist showed no ill effects from this exposure because if we multiple the energy in joules of exposure per second,

1.31*10^-11, by the total amount of seconds of exposure, 5.26*10^6s, we find that he was only exposed to 6.9*10^-5 joules of radiation throughout the span of two years. This is a very small amount of radiation for such a long span of time.

In order to plug in the values for this equation, we must convert the given MeV to Joules with the known conversion rate. Similarly, we must convert Joules to amu with another known conversion rate. Then we can plug in the values and multiply by c^2 but we must not forget to multiple the amu by the conversion rate to kg in order to yield Joules. After all of this is done, we multiple the amount of Joules of exposure per second by the total amount of exposure in seconds in order to find out the total amount of exposure over the two year span.

21.2: Patterns of Nuclear Stability

Q21.2.1

How do chemical reactions compare with nuclear reactions with respect to mass changes? Does either type of reaction violate the law of conservation of mass? Explain your answers.

Q21.2.2

Why is the amount of energy released by a nuclear reaction so much greater than the amount of energy released by a chemical reaction?

Q21.2.3

Explain why the mass of an atom is less than the sum of the masses of its component particles.

Q21.2.4

The stability of a nucleus can be described using two values. What are they, and how do they differ from each other?

Q21.2.5

In the days before true chemistry, ancient scholars (alchemists) attempted to find the philosopher's stone, a material that would enable them to turn lead into gold. Is the conversion of Pb → Au energetically favorable? Explain why or why not.

Q21.2.6

Describe the energy barrier to nuclear fusion reactions and explain how it can be overcome.

Q21.2.7

Imagine that the universe is dying, the stars have burned out, and all the elements have undergone fusion or radioactive decay. What would be the most abundant element in this future universe? Why?

Q21.2.8

Numerous elements can undergo fission, but only a few can be used as fuels in a reactor. What aspect of nuclear fission allows a nuclear chain reaction to occur?

Q21.2.9

How are transmutation reactions and fusion reactions related? Describe the main impediment to fusion reactions and suggest one or two ways to surmount this difficulty.

Q21.2.10

Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules.

a. $^{238}\text{Pa} \rightarrow ? + \beta^-$
b. $^{216}\text{Fr} \rightarrow ? + \alpha$
c. $^{199}\text{Bi} \rightarrow ? + \beta^+$

Q21.2.22

Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules.

a. $^{194}\text{Tl} \rightarrow ? + \beta^+$
b. $^{171}\text{Pt} \rightarrow ? + \alpha$
c. $^{214}\text{Pb} \rightarrow ? + \beta^-$

Q21.2.23

Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules per mole.

a. $^{234}_{91}\text{Pa} \rightarrow ? + {}^{0}_{-1}\beta$
b. $^{226}_{88}\text{Ra} \rightarrow ? + {}^{4}_{2}\alpha$

Q21.2.24

Using the information provided in Chapter 33, complete each reaction and then calculate the amount of energy released from each in kilojoules per mole.

a. $^{60}_{27}\text{Co} \rightarrow ? + {}^{0}_{-1}\beta$ (The mass of cobalt-60 is 59.933817 amu.)
b. technicium-94 (mass = 93.909657 amu) undergoing fission to produce chromium-52 and potassium-40

Q21.2.25

Using the information provided in Chapter 33, predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.

a. the beta decay of bismuth-208 (mass = 207.979742 amu)
b. the formation of lead-206 by alpha decay

Q21.2.26

Using the information provided, predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.

a. alpha decay of oxygen-16
b. alpha decay to produce chromium-52

Q21.2.27

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{87}Sr if the measured

mass of ^{87}Sr is 86.908877 amu.

a. the calculated mass
b. the mass defect
c. the nuclear binding energy
d. the nuclear binding energy per nucleon

Q21.2.30

The experimentally determined mass of ^{29}S is 28.996610 amu. Find each of the following.

a. the calculated mass
b. the mass defect
c. the nuclear binding energy
d. the nuclear binding energy per nucleon

Q21.2.31

Calculate the amount of energy that is released by the neutron-induced fission of ^{235}U to give ^{141}Ba, ^{92}Kr (mass = 91.926156 amu), and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.

Q21.2.31

Calculate the amount of energy that is released by the neutron-induced fission of ^{235}U to give ^{90}Sr, ^{143}Xe, and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.

Q21.2.33

Calculate the amount of energy released or required by the fusion of helium-4 to produce the unstable beryllium-8 (mass = 8.00530510 amu). Report your answer in kilojoules per mole. Do you expect this to be a spontaneous reaction?

Q21.2.34

Calculate the amount of energy released by the fusion of ^{6}Li and deuterium to give two helium-4 nuclei. Express your answer in electronvolts per atom and kilojoules per mole.

Q21.2.35

How much energy is released by the fusion of two deuterium nuclei to give one tritium nucleus and one proton? How does this amount compare with the energy released by the fusion of a deuterium nucleus and a tritium nucleus, which is accompanied by ejection of a neutron? Express your answer in megaelectronvolts and kilojoules per mole. Pound for pound, which is a better choice for a fusion reactor fuel mixture?

Numerical Answers

1

a. $^{238}_{91}\mathrm{Pa} \rightarrow {}^{238}_{92}\mathrm{U} + {}^{0}_{-1}\beta$; -5.540×10^{-16} kJ
b. $^{216}_{87}\mathrm{Fr} \rightarrow {}^{212}_{85}\mathrm{At} + {}^{4}_{2}\alpha$; -1.470×10^{-15} kJ
c. $^{199}_{83}\mathrm{Bi} \rightarrow {}^{199}_{82}\mathrm{Pb} + {}^{0}_{+1}\beta$; -5.458×10^{-16} kJ

3.

a. $^{234}_{91}\mathrm{Pa} \rightarrow {}^{234}_{92}\mathrm{U} + {}^{0}_{-1}\beta$; 2.118 × 10^8 kJ/mol
b. $^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + {}^{4}_{2}\alpha$; 4.700 × 10^8 kJ/mol

5.

a. The beta decay of bismuth-208 to polonium is endothermic (ΔE = 1.400 MeV/atom, 1.352 × 10^8 kJ/mol).
b. The formation of lead-206 by alpha decay of polonium-210 is exothermic (ΔE = −5.405 MeV/atom, −5.218 × 10^8 kJ/mol).

7. 757 MeV/atom, 8.70 MeV/nucleon

9.

a. 53.438245 amu
b. 0.496955 amu
c. 463 MeV/atom
d. 8.74 MeV/nucleon

11. −173 MeV/atom; 1.67 × 10^{10} kJ/mol

13. ΔE = + 9.0 × 10^6 kJ/mol beryllium-8; no

15. D–D fusion: ΔE = −4.03 MeV/tritium nucleus formed = −3.89 × 10^8 kJ/mol tritium; D–T fusion: ΔE = −17.6 MeV/tritium nucleus = −1.70 × 10^9 kJ/mol; D–T fusion

21.3: Nuclear Transmutations

Q21.3.1

Why do scientists believe that hydrogen is the building block of all other elements? Why do scientists believe that helium-4 is the building block of the heavier elements?

Q21.3.2

How does a star produce such enormous amounts of heat and light? How are elements heavier than Ni formed?

Q21.3.3

Propose an explanation for the observation that elements with even atomic numbers are more abundant than elements with odd atomic numbers.

S21.3.3

The raw material for all elements with Z > 2 is helium (Z = 2), and fusion of helium nuclei will always produce nuclei with an even number of protons.

Q21.3.4

During the lifetime of a star, different reactions that form different elements are used to power the fusion furnace that keeps a star “lit.” Explain the different reactions that dominate in the different stages of a star’s life cycle and their effect on the temperature of the star.

Q21.3.5

A line in a popular song from the 1960s by Joni Mitchell stated, “We are stardust….” Does this statement have any merit or is it just poetic? Justify your answer.

Q21.3.6

If the laws of physics were different and the primary element in the universe were boron-11 (Z = 5), what would be the next four most abundant elements? Propose nuclear reactions for their formation.

Q21.3.7

Write a balanced nuclear reaction for the formation of each isotope.

a. ^{27}Al from two ^{12}C nuclei
b. ^{9}Be from two ^{4}He nuclei

Q21.3.8

At the end of a star’s life cycle, it can collapse, resulting in a supernova explosion that leads to the formation of heavy elements by multiple neutron-capture events. Write a balanced nuclear reaction for the formation of each isotope during such an explosion.

a. ^{106}Pd from nickel-58
b. selenium-79 from iron-56

Q21.3.9

When a star reaches middle age, helium-4 is converted to short-lived beryllium-8 (mass = 8.00530510 amu), which reacts with another helium-4 to produce carbon-12. How much energy is released in each reaction (in megaelectronvolts)? How many atoms of helium must be “burned” in this process to produce the same amount of energy obtained from the fusion of 1 mol of hydrogen atoms to give deuterium?

21.4: Rates of Radioactive Decay

Q21.4.1

What do chemists mean by the half-life of a reaction?

Q21.4.2

If a sample of one isotope undergoes more disintegrations per second than the same number of atoms of another isotope, how do their half-lives compare?

Q21.4.3

Half-lives for the reaction A + B → C were calculated at three values of $[A]_0$, and [B] was the same in all cases. The data are listed in the following table:

$[A]_0$ (M)	$t_{½}$ (s)
0.50	420
0.75	280

$[A]_0$ (M)	$t_{½}$ (s)
1.00	210

Does this reaction follow first-order kinetics? On what do you base your answer?

S21.4.3

1. No; the reaction is second order in A because the half-life decreases with increasing reactant concentration according to $t_{1/2} = 1/k[A_0]$.

Q21.4.4

Ethyl-2-nitrobenzoate ($NO_2C_6H_4CO_2C_2H_5$) hydrolyzes under basic conditions. A plot of $[NO_2C_6H_4CO_2C_2H_5]$ versus t was used to calculate $t_{½}$, with the following results:

$[NO_2C_6H_4CO_2C_2H_5]$ (M/cm^3)	$t_{½}$ (s)
0.050	240
0.040	300
0.030	400

Is this a first-order reaction? Explain your reasoning.

Q21.4.5

Azomethane ($CH_3N_2CH_3$) decomposes at 600 K to C_2H_6 and N_2. The decomposition is first order in azomethane. Calculate $t_{½}$ from the data in the following table:

Time (s)	$P_{CH_3N_2CH_3}$ (atm)
0	8.2×10^{-2}
2000	3.99×10^{-2}
4000	1.94×10^{-2}

How long will it take for the decomposition to be 99.9% complete?

S21.4.5

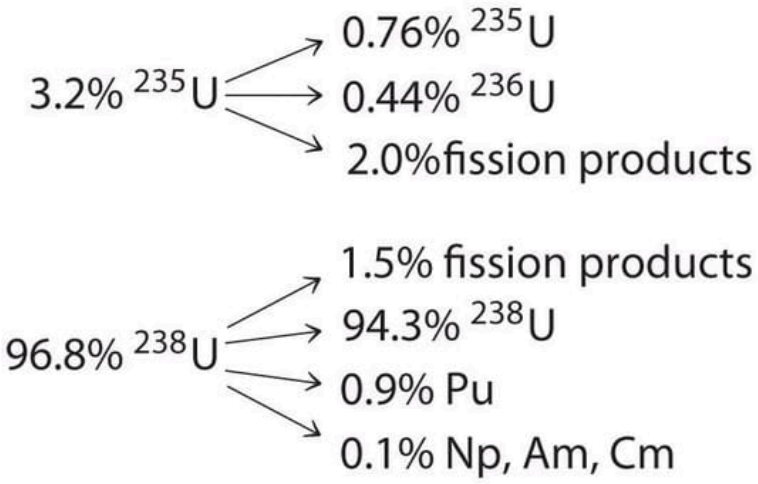
$t_{1/2} = 1.92 \times 10^3$ s or 1920 s; 19100 s or 5.32 hrs.

Q21.4.6

The first-order decomposition of hydrogen peroxide has a half-life of 10.7 h at 20°C. What is the rate constant (expressed in s^{-1}) for this reaction? If you started with a solution that was 7.5×10^{-3} M H_2O_2, what would be the initial rate of decomposition (M/s)? What would be the concentration of H_2O_2 after 3.3 h?

Application Problems

1. Until the 1940s, uranium glazes were popular on ceramic dishware. One brand, Fiestaware, had bright orange glazes that could contain up to 20% uranium by mass. Although this practice is less common today due to the negative association of radiation, it is still possible to buy Depression-era glassware that is quite radioactive. Aqueous solutions in contact with this "hot" glassware can reach uranium concentrations up to 10 ppm by mass. If 1.0 g of uranium undergoes 1.11×10^7 decays/s, each to an α particle with an energy of 4.03 MeV, what would be your exposure in rem and rad if you drank 1.0 L of water that had been sitting for an extended time in a Fiestaware pitcher? Assume that the water and contaminants are excreted only after 18 h and that you weigh 70.0 kg.
2. Neutrography is a technique used to take the picture of an object using a beam of neutrons. How does the penetrating power of a neutron compare with alpha, beta, and gamma radiation? Do you expect similar penetration for protons? How would the biological damage of each particle compare with the other types of radiation? (Recall that a neutron's mass is approximately 2000 times the mass of an electron.)
3. Spent fuel elements in a nuclear reactor contain radioactive fission products in addition to heavy metals. The conversion of nuclear fuel in a reactor is shown here:



   Neglecting the fission products, write balanced nuclear reactions for the conversion of the original fuel to each product.

4. The first atomic bomb used ^{235}U as a fissile material, but there were immense difficulties in obtaining sufficient quantities of pure ^{235}U. A second fissile element, plutonium, was discovered in 1940, and it rapidly became important as a nuclear fuel. This element was produced by irradiating ^{238}U with neutrons in a nuclear reactor. Complete the series that produced plutonium, all isotopes of which are fissile:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow \ \mathrm{U} \rightarrow \ \mathrm{Np} \rightarrow \ \mathrm{Pu}$$

5. Boron neutron capture therapy is a potential treatment for many diseases. As the name implies, when boron-10, one of the naturally occurring isotopes of boron, is bombarded with neutrons, it absorbs a neutron and emits an α particle. Write a balanced nuclear reaction for this reaction. One advantage of this process is that neutrons cause little damage on their own, but when they are absorbed by boron-10, they can cause localized emission of alpha radiation. Comment on the utility of this treatment and its potential difficulties.

6. An airline pilot typically flies approximately 80 h per month. If 75% of that time is spent at an altitude of about 30,000 ft, how much radiation is that pilot receiving in one month? over a 30 yr career? Is the pilot receiving toxic doses of radiation?

7. At a breeder reactor plant, a 72 kg employee accidentally inhaled 2.8 mg of ^{239}Pu dust. The isotope decays by alpha decay and has a half-life of 24,100 yr. The energy of the emitted α particles is 5.2 MeV, and the dust stays in the employee's body for 18 h.

a. How many plutonium atoms are inhaled?
b. What is the energy absorbed by the body?
c. What is the physical dose in rads?
d. What is the dose in rems? Will the dosage be fatal?

8. For many years, the standard source for radiation therapy in the treatment of cancer was radioactive ^{60}Co, which undergoes beta decay to ^{60}Ni and emits two γ rays, each with an energy of 1.2 MeV. Show the sequence of nuclear reactions. If the half-life for beta decay is 5.27 yr, how many ^{60}Co nuclei are present in a typical source undergoing 6000 dps that is used by hospitals? The mass of ^{60}Co is 59.93 amu.

9. It is possible to use radioactive materials as heat sources to produce electricity. These radioisotope thermoelectric generators (RTGs) have been used in spacecraft and many other applications. Certain Cold War–era Russian-made RTGs used a 5.0 kg strontium-90 source. One mole of strontium-90 releases β particles with an energy of 0.545 MeV and undergoes 2.7×10^{13} decays/s. How many watts of power are available from this RTG (1 watt = 1 J/s)?

10. Potassium consists of three isotopes (potassium-39, potassium-40, and potassium-41). Potassium-40 is the least abundant, and it is radioactive, decaying to argon-40, a stable, nonradioactive isotope, by the emission of a β particle with a half-life of precisely 1.25×10^9 yr. Thus the ratio of potassium-40 to argon-40 in any potassium-40–containing material can be used to date the sample. In 1952, fragments of an early hominid, Meganthropus, were discovered near Modjokerto in Java. The bone fragments were lying on volcanic rock that was believed to be the same age as the bones. Potassium–argon dating on samples of the volcanic material showed that the argon-40-to-potassium-40 molar ratio was 0.00281:1. How old were the rock fragments? Could the bones also be the same age? Could radiocarbon dating have been used to date the fragments?

Answers

1. 6.6×10^{-3} rad; 0.13 rem
3. $$\begin{aligned}
{}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} &\rightarrow {}^{236}_{92}\mathrm{U} + \gamma \\
{}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} &\rightarrow {}^{239}_{92}\mathrm{U} + \gamma \\
{}^{239}_{92}\mathrm{U} &\rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta \\
{}^{239}_{93}\mathrm{Np} &\rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta \\
{}^{239}_{94}\mathrm{Pu} &\rightarrow {}^{239}_{95}\mathrm{Am} + {}^{0}_{-1}\beta \\
{}^{239}_{95}\mathrm{Am} &\rightarrow {}^{239}_{96}\mathrm{Cm} + {}^{0}_{-1}\beta
\end{aligned}$$
7.
   a. 7.1×10^{18} atoms of Pu
   b. 0.35 J
   c. 0.49 rad
   d. 9.8 rem; this dose is unlikely to be fatal.
9. 130 W

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21.S: Nuclear Chemistry (Summary)

21.1: Radioactivity

- ◦ **nucleons** – neutron and proton
  - ◦ all atoms of a given element have the same number of protons, atomic number
  - ◦ **isotopes** – atoms with the same atomic number but different mass numbers
  - ◦ three isotopes of uranium: uranium-233, uranium-235, uranium-238
  - ◦ $^{233}_{92}\mathrm{U}, {}^{235}_{92}\mathrm{U}, {}^{238}_{92}\mathrm{U}$ (superscript is mass number, subscript atomic number)
  - ◦ radionuclides – nuclei that are radioactive
  - ◦ radioisotopes – atoms containing radionuclides

21.1.1 Nuclear Equations

- ◦ **alpha particles** – helium-4 particles
  - ◦ **alpha radiation** – stream of alpha particles
  - ◦ emission of radiation is one way that an unstable nucleus is transformed into a more stable one
  - ◦ $^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$
  - ◦ superscript = mass number
  - ◦ subscript = atomic number
  - ◦ **radioactive decay** – when a nucleus spontaneously decomposes
  - ◦ sum of the mass numbers is the same on both sides of the equation
  - ◦ sum of the atomic numbers same on both sides of the equation
  - ◦ radioactive properties of the nucleus are independent of the state of chemical combination of the atom
  - ◦ chemical form does not matter when writing nuclear equations

21.1.2 Types of Radioactive Decay

- three most common type of radioactive decay: alpha(α), beta(β), and gamma(γ) radiation

Types of Radiation

Property	α	β	γ
Charge	2+	1-	0
Mass	6.64×10^{-24} g	9.11×10^{-28} g	0
Relative penetrating power	1	100	10,000
Nature of radiation	$^{2}_{4}\mathrm{He}$ nuclei	electrons	High-energy photons

- ◦ **beta particles** – high speed electrons emitted by an unstable nucleus
  - ◦ $^{131}_{53}\mathrm{I} \rightarrow {}^{131}_{54}\mathrm{Xe} + {}^{0}_{-1}\mathrm{e}$
  - ◦ beta decay results in increasing the atomic number
  - ◦ $^{1}_{0}\mathrm{n} \rightarrow {}^{1}_{1}\mathrm{p} + {}^{0}_{-1}\mathrm{e}$
  - ◦ **gamma radiation** – high-energy protons
  - ◦ gamma radiation does not change atomic number or mass number or a nucleus
  - ◦ almost always accompanies other radioactive emission
  - ◦ represents the energy lost when the remaining nucleons reorganize into more stable arrangements
  - ◦ **positron** – particle that has same mass as an electron but opposite charge

- represented by ${}^{0}_{1}e$
- emission of a positron has effect of converting a proton to a neutron ⇨ decreasing atomic number of nucleus by 1
- **electron capture** – the capture by the nucleus of an inner-shell electron from the electron cloud surrounding the nucleus
- has effect of converting a proton to neutron
- ${}^{1}_{1}p + {}^{0}_{-1}e \rightarrow {}^{1}_{0}n$

Particle	Symbol
Neutron	${}^{1}_{0}\mathrm{n}$
Proton	${}^{1}_{1}\mathrm{H}$ or ${}^{1}_{1}\mathrm{p}$
Electron	${}^{0}_{-1}\mathrm{e}$
Alpha Particle	${}^{4}_{2}\mathrm{He}$ or ${}^{4}_{2}\alpha$
Beta Particle	${}_{-1}{}^{0}\ \mathrm{e}$ or ${}^{0}_{-1}\beta$
Positron	${}^{0}_{1}\mathrm{e}$

21.2: Patterns of Nuclear Stability

21.2.1 Neutron-to-Proton Ratio

- **strong nuclear force** – a strong force of attraction between a large number of protons in the small volume of the nucleus
- stable nuclei with low atomic numbers up to 20 have nearly equal number of neutrons and protons
- for higher atomic numbers, the number of neutrons are greater than the number of protons
- the neutron-to-proton ratio of stable nuclei increase with increasing atomic number
- **belt of stability** – area where all stable nuclei are found
  - ends at bismuth
  - all nuclei with 84 or more protons are radioactive
  - an even number of protons and neutrons is more stable than an odd number
- determining type of radioactive decay
  - 1) nuclei above the belt of stability
  - high neutron-to-proton ratios
  - move toward belt of stability by emitting a beta particle
  - decreases the number of neutrons and increases the number of protons in a nucleus
  - 2) nuclei below the belt of stability
  - low neutron-to-proton ratios
  - move toward belt of stability by positron emission or electron capture
  - increase number of neutrons and decrease the number of protons
  - positron emission more common with lower nuclear charges
  - electron capture becomes more common with increasing nuclear charge
  - 3) nuclei with atomic numbers Image81.gif84
  - alpha emission
  - decreases both number of neutrons and protons by 2

21.2.2 Radioactive Series

- some nuclei cannot game stability by a single emission
- radioactive series or nuclear disintegration series – series of nuclear reactions that begin with an unstable nucleus to a stable one
- three types of radioactive series found in nature
  - uranium-238 to lead-206, uranium-235 to leat-207, and thorium-232 to lead-208

21.2.3 Further Observations

- ◦ nuclei with 2, 8, 20, 28, 50, or 82 protons or 2, 8, 20, 28, 50, 82, or 126 neutrons are more stable than with nuclei without these numbers
  ◦ numbers called magic numbers
  ◦ nuclei with even number of protons and neutrons more stable than with odd number of protons and neutrons
  ◦ observations made in terms of the shell model of the nucleus
    ▪ nucleons reside in shells
  ◦ magic numbers represent closed shells in nuclei

21.3: Nuclear Transmutations

- ◦ **nuclear transmutations** – nuclear reactions caused by the collision of one nucleus with a neutron or by another nucleus
  ◦ first conversion of one nucleus into another performed by Ernest Rutherford in 1919
  ◦ converted nitrogen-14 to oxygen-17
  ◦ $^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \rightarrow ^{17}_{8}\mathrm{O} + ^{1}_{1}\mathrm{H}$
  ◦ $^{14}_{7}\mathrm{N}(\alpha, \mathrm{p})^{17}_{8}\mathrm{O}$

21.3.1 Using Charged Particles

- ◦ **particle accelerators** – used to accelerate particles at very high speeds
  ◦ cyclotron, and synchrotron

21.3.2 Using Neutrons

- neutrons do not need to be accelerated

21.3.4 Transuranium Elements

- **transuranium elements** – elements with atomic numbers above 92 that are produced by artificial transmutations

21.4: Rates of Radioactive Decay

- ◦ radioactive decay is a first-order process
  ◦ has characteristic of half life, which is the time required for half of any given quantity of a substance to react
  ◦ half-life unaffected by external conditions

21.4.1 Dating

- ◦ radiocarbon dating assumes that the ratio of carbon-14 to carbon-12 in the atmosphere has been constant for at least 50,000 years
  ◦ age of rocks can be determined by ratio of uranium-238 to lead-206

21.4.2 Calculations Based on Half-life

- ◦ rate = kN
  ◦ k = decay constant, N = nuclei
  ◦ $$\ln \frac{N_t}{N_o} = -kt$$
  ◦ t = time interval of decay, k = decay constant, N_0 = initial number of nuclei at time zero, N_t = number remaining after time interval

- $$k = \frac{0.693}{t_{1/2}}$$

21.5 Detection of Radioactivity

- **Geiger counter** – device used to measure and detect radioactivity
- Based on ionization of matter caused by radiation
- **Phosphors** – substances that give off light when exposed to radiation
- **Scintillation counter** – used to detect and measure radiation based on tiny flashes of light produced when radiation strikes a suitable phosphor

21.5.1 Radiotracers

- radioisotopes can be used to follow an element through its chemical reactions
- isotopes of same element have same properties
- **radiotracer** – radioisotopes used to trace an element

21.6: Energy Changes in Nuclear Reactions

$$E = mc^2$$

E = energy, m = mass, c = speed of light

If system loses mass, it loses energy (exothermic)

If system gains mass, it gains energy (endothermic)

21.6.1 Nuclear Binding Energies

- masses of nuclei always less than masses of individual nucleons
- **mass defect** – mass difference between a nucleus and its constituent nucleons
- energy is needed to break nucleus into separated protons and neutrons, addition of energy must also have an increase in mass
- nuclear binding energy – energy required to separate a nucleus into its individual nucleons
  - the larger to nuclear binding energy the more stable the nucleus toward decomposition
- **fission** – energy produced when heavy nuclei split
- **fusion** – energy produced when light nuclei fuse

21.7: Nuclear Fission

- fission and fusion both exothermic
- chain reaction – reaction in which the neutrons produced in one fission cause further fission reactions
- in order for a fission chain reaction to occur, the sample of fissionable material must have a certain minimum mass
- **critical mass** – amount of fissionable material large enough to maintain the chain reaction with a constant rate of fission
- **supercritical mass** – mass in excess of a critical mass

21.7.1 Nuclear Reactors

- nuclear reactors the fission is controlled to generate a constant power
- reactor core consists of fissionable fuel, control rods, a moderator, and cooling fluid
- fission products are extremely radioactive and are thus hard to store
- about 20 half-lives needed for products to react acceptable levels for biological exposure

21.8: Nuclear Fusion

- fusion is appealing because of availability of light isotopes and fusion products are not radioactive
- high energies needed to overcome attraction of nuclei
- **thermonuclear reactions** – fusion reactions
- lowest temperature required is about 40,000,000 K

21.9: Biological Effects of Radiation

- when matter absorbs radiation, the energy of the radiation can cause either excitation or ionization
- ionization radiation more harmful than nonionization radiation
- most of energy of radiation absorbed by water molecules
- **free radical** – a substance with one ore more unpaired electrons
- can attack other biomolecules to produce more free radicals
- gamma rays most dangerous
- tissues that take most damage are the ones that reproduce at a rapid rate
- bone marrow, blood forming tissues, lymph nodes

21.9.1 Radiation Doses

-
  - becquerel (Bq) – SI unit for activity of the radiation source; rate at which nuclear disintegrations are occurring
  - 1 (Bq) = 1 nuclear disintegration/s
  - curie (Ci) = 3.7×10^{10} disintegrations/s = rate of decay of 1g of radium
  - two units used to measure amount of exposure to radiation: gray (Gy) and rad
  - gray – SI unit of absorbed dose = absorption of 1 J of energy per kilogram of tissue
  - rad (radiation absorbed dose) – absorption of 1×10^{-2} J of energy per kilogram of tissue
  - 1 Gy = 100 rads
  - relative biological effectiveness – RBE
    - 1 for gamma and beta radiation, 10 for alpha radiation
    - exact value varies with dose rate, total dose, and type of tissue affected
    - rem (roentgen equivalent for man) – product of the radiation dose in rads and the RBE of the radiation gibes the effective dosage
    - rem is unit of radiation damage that is usually used in medicine
    - number of rems = (number of rads)(RBE)
  - Sievert (Sv) – SI unit for dosage
    - 1 Sv = 100 rem
    - annual exposure = 360mrem

21.9.2 Radon

-
  - radon exposure estimated to account for more than half annual exposure
  - half-life of radon is 3.82 days
  - decays into radioisotope polonium
  - atoms of polonium can be trapped in lungs giving out alpha radiation causing lung cancer
  - recommended levels of radon-222 in homes is to be less than 4 pCi per liter of air

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22: CHEMISTRY OF THE NONMETALS

The line that divides metals from nonmetals in the periodic table crosses the *p* block diagonally. As a result, the differences between metallic and nonmetallic properties are evident within each group, even though all members of each group have the same valence electron configuration. The *p* block is the only portion of the periodic table where we encounter the inert-pair effect. Moreover, as with the *s*-block elements, the chemistry of the lightest member of each group in the *p* block differs sharply from that of its heavier congeners but is similar to that of the element immediately below and to the right of it in the next group. Thus diagonal similarities in chemistry are seen across the *p* block.

A nonmetal is a chemical element that mostly lacks metallic attributes. Physically, nonmetals tend to be highly volatile (easily vaporized), have low elasticity, and are good insulators of heat and electricity; chemically, they tend to have high ionization energy and electronegativity values, and gain or share electrons when they react with other elements or compounds. Seventeen elements are generally classified as nonmetals; most are gases (hydrogen, helium, nitrogen, oxygen, fluorine, neon, chlorine, argon, krypton, xenon and radon); one is a liquid (bromine); and a few are solids (carbon, phosphorus, sulfur, selenium, and iodine).

As you study the periodic trends in properties and the reactivity of the elements in groups 13–18, you will learn how “cobalt blue” glass, rubies, and sapphires are made and why the US military became interested in using boron hydrides as rocket fuels but then abandoned its effort. You will also discover the source of diamonds on Earth, why silicon-based life-forms are likely to exist only in science fiction, and why most compounds with N–N bonds are potentially explosive. You will also learn why phosphorus can cause a painful and lethal condition known as “phossy jaw” and why selenium is used in photocopiers.

22.1: General Concepts- Periodic Trends and Reactions

22.2: Hydrogen

22.3: Group 18- Noble Gases

22.4: Group 17- The Halogens

22.5: Oxygen

22.6: The Other Group 16 Elements- S, Se, Te, and Po

22.7: Nitrogen

22.8: The Other Group 15 Elements - P, AS, Sb, and Bi

22.9: Carbon

22.10: The Other Group 14 Elements- Si, Ge, Sn, and Pb

22.11: Boron

22.E: Chemistry of the Nonmetals (Exercises)

22.S: Chemistry of the Nonmetals (Summary)

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22.1: General Concepts- Periodic Trends and Reactions

Learning Objectives

- To know important periodic trends in several atomic properties.

As we begin our summary of periodic trends, recall that the single most important unifying principle in understanding the chemistry of the elements is the systematic increase in atomic number, accompanied by the orderly filling of atomic orbitals by electrons, which leads to periodicity in such properties as atomic and ionic size, ionization energy, electronegativity, and electron affinity. The same factors also lead to periodicity in valence electron configurations, which for each group results in similarities in oxidation states and the formation of compounds with common stoichiometries.

The most important periodic trends in atomic properties are summarized in Figure 22.1.1. Recall that these trends are based on periodic variations in a single fundamental property, the **effective nuclear charge** (Z_{eff}), which increases from left to right and from top to bottom in the periodic table.

The diagonal line in Figure 22.1.1 separates the metals (to the left of the line) from the nonmetals (to the right of the line). Because metals have relatively low electronegativities, they tend to lose electrons in chemical reactions to elements that have relatively high electronegativities, forming compounds in which they have positive oxidation states. Conversely, nonmetals have high electronegativities, and they therefore tend to gain electrons in chemical reactions to form compounds in which they have negative oxidation states. The semimetals lie along the diagonal line dividing metals and nonmetals. It is not surprising that they tend to exhibit properties and reactivities intermediate between those of metals and nonmetals. Because the elements of groups 13, 14, and 15 span the diagonal line separating metals and nonmetals, their chemistry is more complex than predicted based solely on their valence electron configurations.

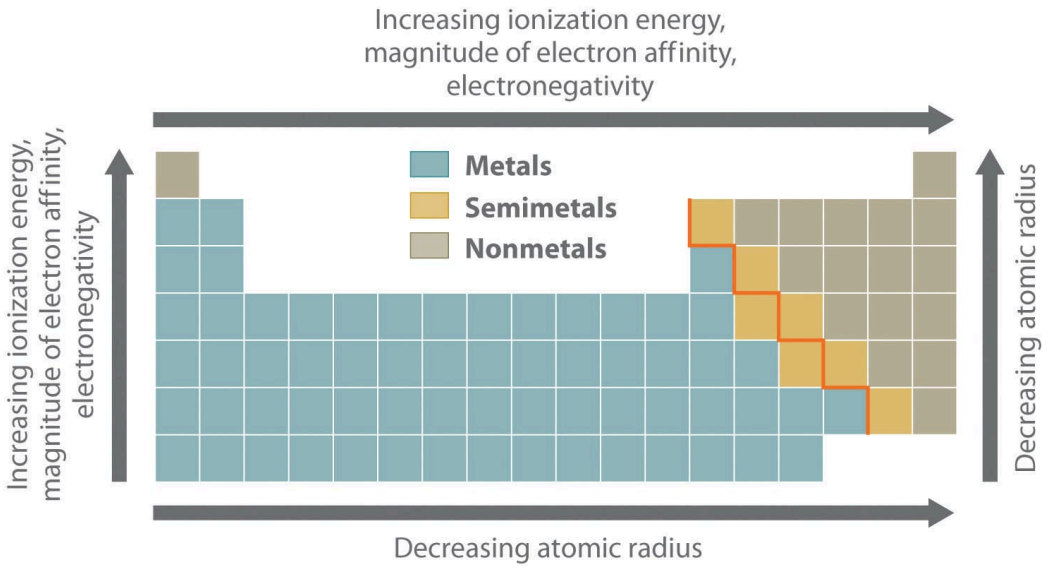


Figure 22.1.1: Summary of Periodic Trends in Atomic Properties. Ionization energies, the magnitude of electron affinities, and electronegativities generally increase from left to right and from bottom to top. In contrast, atomic size decreases from left to right and from bottom to top. Consequently, the elements in the upper right of the periodic table are the smallest and most electronegative; the elements in the bottom left are the largest and least electronegative. The semimetals lie along the diagonal line separating the metals from the nonmetals and exhibit intermediate properties.

Unique Chemistry of the Lightest Elements

The chemistry of the second-period element of each group (n = 2: Li, Be, B, C, N, O, and F) differs in many important respects from that of the heavier members, or congeners, of the group. Consequently, the elements of the third period (n = 3: Na, Mg, Al,

Si, P, S, and Cl) are generally more representative of the group to which they belong. The anomalous chemistry of second-period elements results from three important characteristics: small radii, energetically unavailable d orbitals, and a tendency to form pi (π) bonds with other atoms.

> In contrast to the chemistry of the second-period elements, the chemistry of the third-period elements is more representative of the chemistry of the respective group.

Due to their small radii, second-period elements have electron affinities that are less negative than would be predicted from general periodic trends. When an electron is added to such a small atom, increased electron–electron repulsions tend to destabilize the anion. Moreover, the small sizes of these elements prevent them from forming compounds in which they have more than four nearest neighbors. Thus BF_3 forms only the four-coordinate, tetrahedral BF_4^- ion, whereas under the same conditions AlF_3 forms the six-coordinate, octahedral AlF_6^{3-} ion. Because of the smaller atomic size, simple binary ionic compounds of second-period elements also have more covalent character than the corresponding compounds formed from their heavier congeners. The very small cations derived from second-period elements have a high charge-to-radius ratio and can therefore polarize the filled valence shell of an anion. As such, the bonding in such compounds has a significant covalent component, giving the compounds properties that can differ significantly from those expected for simple ionic compounds. As an example, LiCl, which is partially covalent in character, is much more soluble than NaCl in solvents with a relatively low dielectric constant, such as ethanol (ε = 25.3 versus 80.1 for H_2O).

Because d orbitals are never occupied for principal quantum numbers less than 3, the valence electrons of second-period elements occupy 2s and 2p orbitals only. The energy of the 3d orbitals far exceeds the energy of the 2s and 2p orbitals, so using them in bonding is energetically prohibitive. Consequently, electron configurations with more than four electron pairs around a central, second-period element are simply not observed. You may recall that the role of d orbitals in bonding in main group compounds with coordination numbers of 5 or higher remains somewhat controversial. In fact, theoretical descriptions of the bonding in molecules such as SF_6 have been published without mentioning the participation of d orbitals on sulfur. Arguments based on d-orbital availability and on the small size of the central atom, however, predict that coordination numbers greater than 4 are unusual for the elements of the second period, which is in agreement with experimental results.

One of the most dramatic differences between the lightest main group elements and their heavier congeners is the tendency of the second-period elements to form species that contain multiple bonds. For example, N is just above P in group 15: N_2 contains an N≡N bond, but each phosphorus atom in tetrahedral P_4 forms three P–P bonds. This difference in behavior reflects the fact that within the same group of the periodic table, the relative energies of the π bond and the sigma (σ) bond differ. A C=C bond, for example, is approximately 80% stronger than a C–C bond. In contrast, an Si=Si bond, with less p-orbital overlap between the valence orbitals of the bonded atoms because of the larger atomic size, is only about 40% stronger than an Si–Si bond. Consequently, compounds that contain both multiple and single C to C bonds are common for carbon, but compounds that contain only sigma Si–Si bonds are more energetically favorable for silicon and the other third-period elements.

Another important trend to note in main group chemistry is the chemical similarity between the lightest element of one group and the element immediately below and to the right of it in the next group, a phenomenon known as the diagonal effect (Figure 22.1.2) There are, for example, significant similarities between the chemistry of Li and Mg, Be and Al, and B and Si. Both $BeCl_2$ and $AlCl_3$ have substantial covalent character, so they are somewhat soluble in nonpolar organic solvents. In contrast, although Mg and Be are in the same group, $MgCl_2$ behaves like a typical ionic halide due to the lower electronegativity and larger size of magnesium.



Figure 22.1.2: The Diagonal Effect. The properties of the lightest element in a group are often more similar to those of the element below and to the right in the periodic table. For instance, the chemistry of lithium is more similar to that of magnesium in group 2 than it is to the chemistry of sodium, the next member in group 1.

The Inert-Pair Effect

The **inert-pair effect** refers to the empirical observation that the heavier elements of groups 13–17 often have oxidation states that are lower by 2 than the maximum predicted for their group. For example, although an oxidation state of +3 is common for group 13 elements, the heaviest element in group 13, thallium (Tl), is more likely to form compounds in which it has a +1 oxidation state. There appear to be two major reasons for the inert-pair effect: increasing ionization energies and decreasing bond strengths.

> In moving down a group in the p-block, increasing ionization energies and decreasing bond strengths result in an inert-pair effect.

The ionization energies increase because filled (n – 1)d or (n – 2)f subshells are relatively poor at shielding electrons in ns orbitals. Thus the two electrons in the ns subshell experience an unusually high effective nuclear charge, so they are strongly attracted to the nucleus, reducing their participation in bonding. It is therefore substantially more difficult than expected to remove these ns^2electrons, as shown in Table 22.1.1 by the difference between the first ionization energies of thallium and aluminum. Because Tl is less likely than Al to lose its two ns^2 electrons, its most common oxidation state is +1 rather than +3.

Table 22.1.1: Ionization Energies (I) and Average M–Cl Bond Energies for the Group 13 Elements

Element	Electron Configuration	I_1 (kJ/mol)	$I_1 + I_2 + I_3$ (kJ/mol)	Average M–Cl Bond Energy (kJ/mol)
B	[He] $2s^2 2p^1$	801	6828	536
Al	[Ne] $3s^2 3p^1$	578	5139	494
Ga	[Ar] $3d^{10} 4s^2 4p^1$	579	5521	481
In	[Kr] $4d^{10} 5s^2 p^1$	558	5083	439
Tl	[Xe] $4f^{14} 5d^{10} 6s^2 p^1$	589	5439	373

Source of data: John A. Dean, Lange's Handbook of Chemistry, 15th ed. (New York: McGraw-Hill, 1999).

Going down a group, the atoms generally became larger, and the overlap between the valence orbitals of the bonded atoms decreases. Consequently, bond strengths tend to decrease down a column. As shown by the M–Cl bond energies listed in Table

22.1.1, the strength of the bond between a group 13 atom and a chlorine atom decreases by more than 30% from B to Tl. Similar decreases are observed for the atoms of groups 14 and 15.

The net effect of these two factors—increasing ionization energies and decreasing bond strengths—is that in going down a group in the p-block, the additional energy released by forming two additional bonds eventually is not great enough to compensate for the additional energy required to remove the two ns^2 electrons.

Example 22.1.1

Based on the positions of the group 13 elements in the periodic table and the general trends outlined in this section,

a. classify these elements as metals, semimetals, or nonmetals.
b. predict which element forms the most stable compounds in the +1 oxidation state.
c. predict which element differs the most from the others in its chemistry.
d. predict which element of another group will exhibit chemistry most similar to that of Al.

Given: positions of elements in the periodic table

Asked for: classification, oxidation-state stability, and chemical reactivity

Strategy:

From the position of the diagonal line in the periodic table separating metals and nonmetals, classify the group 13 elements. Then use the trends discussed in this section to compare their relative stabilities and chemical reactivities.

Solution

a. Group 13 spans the diagonal line separating the metals from the nonmetals. Although Al and B both lie on the diagonal line, only B is a semimetal; the heavier elements are metals.
b. All five elements in group 13 have an ns^2np^1 valence electron configuration, so they are expected to form ions with a +3 charge from the loss of all valence electrons. The inert-pair effect should be most important for the heaviest element (Tl), so it is most likely to form compounds in an oxidation state that is lower by 2. Thus the +1 oxidation state is predicted to be most important for thallium.
c. Among the main group elements, the lightest member of each group exhibits unique chemistry because of its small size resulting in a high concentration of charge, energetically unavailable d orbitals, and a tendency to form multiple bonds. In group 13, we predict that the chemistry of boron will be quite different from that of its heavier congeners.
d. Within the s and p blocks, similarities between elements in different groups are most marked between the lightest member of one group and the element of the next group immediately below and to the right of it. These elements exhibit similar electronegativities and charge-to-radius ratios. Because Al is the second member of group 13, we predict that its chemistry will be most similar to that of Be, the lightest member of group 2.

Exercise 22.1.1

Based on the positions of the group 14 elements C, Si, Ge, Sn, and Pb in the periodic table and the general trends outlined in this section,

a. classify these elements as metals, semimetals, or nonmetals.
b. predict which element forms the most stable compounds in the +2 oxidation state.
c. predict which element differs the most from the others in its chemistry.
d. predict which element of group 14 will be chemically most similar to a group 15 element.

Answer

a. nonmetal: C; semimetals: Si and Ge; metals: Sn and Pb
b. Pb is most stable as M^{2+}.
c. C is most different.

d. C and P are most similar in chemistry.

Summary

The chemistry of the third-period element in a group is most representative of the chemistry of the group because the chemistry of the second-period elements is dominated by their small radii, energetically unavailable d orbitals, and tendency to form π bonds with other atoms. The most important unifying principle in describing the chemistry of the elements is that the systematic increase in atomic number and the orderly filling of atomic orbitals lead to periodic trends in atomic properties. The most fundamental property leading to periodic variations is the effective nuclear charge (Z_{eff}). Because of the position of the diagonal line separating metals and nonmetals in the periodic table, the chemistry of groups 13, 14, and 15 is relatively complex. The second-period elements (n = 2) in each group exhibit unique chemistry compared with their heavier congeners because of their smaller radii, energetically unavailable d orbitals, and greater ability to form π bonds with other atoms. Increasing ionization energies and decreasing bond strengths lead to the inert-pair effect, which causes the heaviest elements of groups 13–17 to have a stable oxidation state that is lower by 2 than the maximum predicted for their respective groups.

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22.2: Hydrogen

Learning Objectives

- To describe the physical and chemical properties of hydrogen and predict its reactivity.

We now turn from an overview of periodic trends to a discussion of the s-block elements, first by focusing on hydrogen, whose chemistry is sufficiently distinct and important to be discussed in a category of its own. Most versions of the periodic table place hydrogen in the upper left corner immediately above lithium, implying that hydrogen, with a $1s^1$ electron configuration, is a member of group 1. In fact, the chemistry of hydrogen does not greatly resemble that of the metals of Group 1. Indeed, some versions of the periodic table place hydrogen above fluorine in Group 17 because the addition of a single electron to a hydrogen atom completes its valence shell.

> Although hydrogen has an ns^1 electron configuration, its chemistry does not resemble that of the Group 1 metals.

Isotopes of Hydrogen

Hydrogen, the most abundant element in the universe, is the ultimate source of all other elements by the process of nuclear fusion. Table 22.2.1 "The Isotopes of Hydrogen" compares the three isotopes of hydrogen, all of which contain one proton and one electron per atom. The most common isotope is **protium** (^{1}H or H), followed by **deuterium** (^{2}H or D), which has an additional neutron. The rarest isotope of hydrogen is **tritium** (^{3}H or T), which is produced in the upper atmosphere by a nuclear reaction when cosmic rays strike nitrogen and other atoms; it is then washed into the oceans by rainfall. Tritium is radioactive, decaying to ^{3}He with a half-life of only 12.32 years. Consequently, the atmosphere and oceans contain only a very low, steady-state level of tritium. The term hydrogen and the symbol H normally refer to the naturally occurring mixture of the three isotopes.

Table 22.2.1: The Isotopes of Hydrogen

	Protium	Deuterium	Tritium
symbol	$^1_1\mathrm{H}$	$^2_1\mathrm{H}$	$^3_1\mathrm{H}$
neutrons	0	1	2
mass (amu)	1.00783	2.0140	3.01605
abundance (%)	99.9885	0.0115	$\sim 10^{-17}$
half-life (years)	—	—	12.32
boiling point of X_2 (K)	20.28	23.67	25
melting point/boiling point of X_2O (°C)	0.0/100.0	3.8/101.4	4.5/?

The different masses of the three isotopes of hydrogen cause them to have different physical properties. Thus H_2, D_2, and T_2 differ in their melting points, boiling points, densities, and heats of fusion and vaporization. In 1931, Harold Urey and coworkers discovered deuterium by slowly evaporating several liters of liquid hydrogen until a volume of about 1 mL remained. When that remaining liquid was vaporized and its emission spectrum examined, they observed new absorption lines in addition to those previously identified as originating from hydrogen. The natural abundance of tritium, in contrast, is so low that it could not be detected by similar experiments; it was first prepared in 1934 by a nuclear reaction.

Harold Urey (1893–1981)

Urey won the Nobel Prize in Chemistry in 1934 for his discovery of deuterium (^2H). Urey was born and educated in rural Indiana. After earning a BS in zoology from the University of Montana in 1917, Urey changed career directions. He earned his PhD in chemistry at Berkeley with G. N. Lewis and subsequently worked with Niels Bohr in Copenhagen. During World War II, Urey was the director of war research for the Atom Bomb Project at Columbia University. In later years, his research focused on the evolution of life. In 1953, he and his graduate student, Stanley Miller, showed that organic compounds, including amino acids, could be formed by passing an electric discharge through a mixture of compounds thought to be present in the atmosphere of primitive Earth.

Because the normal boiling point of D_2O is 101.4°C (compared to 100.0°C for H_2O), evaporation or fractional distillation can be used to increase the concentration of deuterium in a sample of water by the selective removal of the more volatile H_2O. Thus bodies of water that have no outlet, such as the Great Salt Lake and the Dead Sea, which maintain their level solely by evaporation, have significantly higher concentrations of deuterated water than does lake or seawater with at least one outlet. A more efficient way to obtain water highly enriched in deuterium is by prolonged electrolysis of an aqueous solution. Because a deuteron (D^+) has twice the mass of a proton (H^+), it diffuses more slowly toward the electrode surface. Consequently, the gas evolved at the cathode is enriched in H, the species that diffuses more rapidly, favoring the formation of H_2 over D_2 or HD. Meanwhile, the solution becomes enriched in deuterium. Deuterium-rich water is called heavy water because the density of D_2O (1.1044 g/cm^3 at 25°C) is greater than that of H_2O (0.99978 g/cm^3). Heavy water was an important constituent of early nuclear reactors.

Because deuterons diffuse so much more slowly, D_2O will not support life and is actually toxic if administered to mammals in large amounts. The rate-limiting step in many important reactions catalyzed by enzymes involves proton transfer. The transfer of D^+ is so slow compared with that of H^+ because bonds to D break more slowly than those to H, so the delicate balance of reactions in the cell is disrupted. Nonetheless, deuterium and tritium are important research tools for biochemists. By incorporating these isotopes into specific positions in selected molecules, where they act as labels, or tracers, biochemists can follow the path of a molecule through an organism or a cell. Tracers can also be used to provide information about the mechanism of enzymatic reactions.

Bonding in Hydrogen and Hydrogen-Containing Compounds

The $1s^1$ electron configuration of hydrogen indicates a single valence electron. Because the 1s orbital has a maximum capacity of two electrons, hydrogen can form compounds with other elements in three ways (Figure 22.2.1):

1. **Losing its electron to form a proton (H^+) with an empty 1s orbital.** The proton is a Lewis acid that can accept a pair of electrons from another atom to form an electron-pair bond. In the acid–base reactions, the proton always binds to a lone pair of electrons on an atom in another molecule to form a polar covalent bond. If the lone pair of electrons belongs to an oxygen atom of a water molecule, the result is the hydronium ion (H_3O^+).
2. **Accepting an electron to form a hydride ion (H^-), which has a filled $1s^2$ orbital.** Hydrogen reacts with relatively electropositive metals, such as the alkali metals (group 1) and alkaline earth metals (group 2), to form ionic hydrides, which contain metal cations and H^- ions.
3. **Sharing its electron with an electron on another atom to form an electron-pair bond.** With a half-filled $1s^1$ orbital, the hydrogen atom can interact with singly occupied orbitals on other atoms to form either a covalent or a polar covalent electron-pair bond, depending on the electronegativity of the other atom.

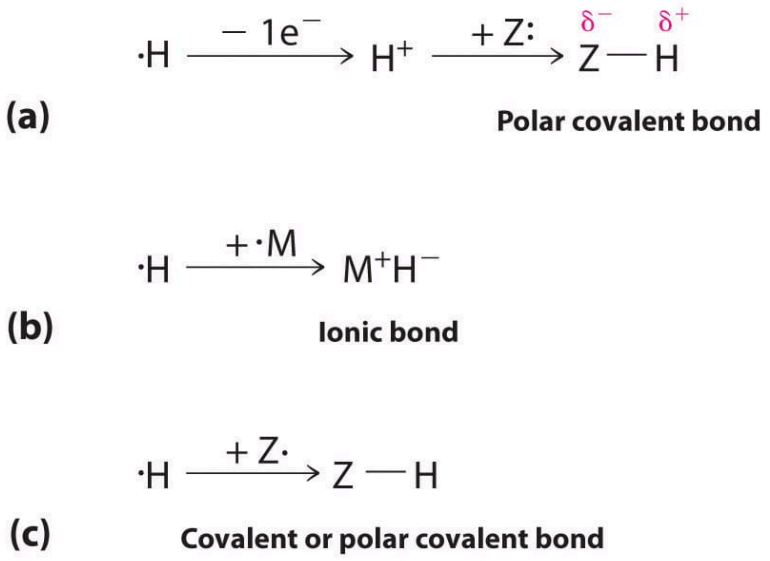


Figure 22.2.1: Three Types of Bonding in Compounds of Hydrogen. Because of its $1s^1$ electron configuration and the fact that the 1s orbital can accommodate no more than two electrons, hydrogen can (a) bond to other elements by losing an electron to form a proton, which can accept a pair of electrons from a more electronegative atom to form a polar covalent bond; (b) gain an electron from an electropositive metal to form a hydride ion, resulting in an ionic hydride; or (c) share its half-filled 1s orbital with a half-filled orbital on another atom to form a covalent or a polar covalent electron-pair bond.

Hydrogen can also act as a bridge between two atoms. One familiar example is the **hydrogen bond**, an electrostatic interaction between a hydrogen bonded to an electronegative atom and an atom that has one or more lone pairs of electrons (Figure 22.2.2). An example of this kind of interaction is the hydrogen bonding network found in water (Figure 22.2.2). Hydrogen can also form a **three-center bond (or electron-deficient bond)**, in which a hydride bridges two electropositive atoms. Compounds that contain hydrogen bonded to boron and similar elements often have this type of bonding. The B–H–B units found in boron hydrides cannot be described in terms of localized electron-pair bonds.

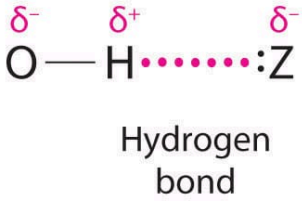


Figure 22.2.2: The Hydrogen Bond. The covalent bond between hydrogen and a very electronegative element, such as nitrogen, oxygen, or fluorine, is highly polar. The resulting partial positive charge on H allows it to interact with a lone pair of electrons on another atom to form a hydrogen bond, which is typically a linear arrangement of the three atoms, with the hydrogen atom placed asymmetrically between the two heavier atoms.

Because the H atom in the middle of such a unit can accommodate a maximum of only two electrons in its 1s orbital, the B–H–B unit can be described as containing a hydride that interacts simultaneously with empty sp^3 orbitals on two boron atoms (Figure 22.2.3). In these bonds, only two bonding electrons are used to hold three atoms together, making them electron-deficient bonds. You encountered a similar phenomenon in the discussion of π bonding in ozone and the nitrite ion. Recall that in both these cases, we used the presence of two electrons in a π molecular orbital extending over three atoms to explain the fact that the two O–O bond distances in ozone and the two N–O bond distances in nitrite are the same, which otherwise can be explained only by the use of resonance structures.

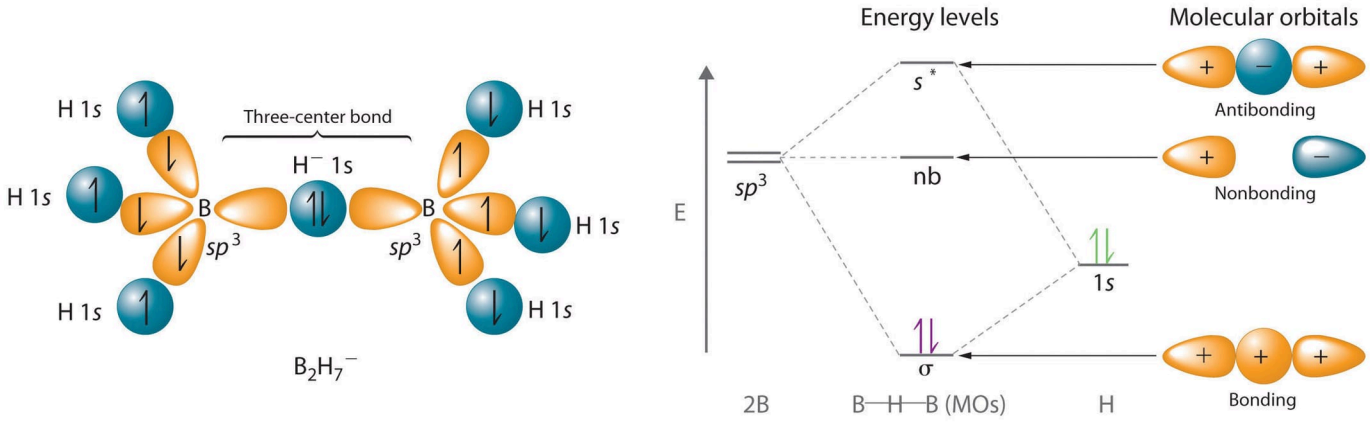


Figure 22.2.3: A Three-Center Bond Uses Two Electrons to Link Three Atoms. In the B–H–B unit shown, a hydride, with a filled 1s orbital, interacts simultaneously with empty sp^3 hybrids on the boron atoms of two BH_3 units to give three molecular orbitals. The two bonding electrons occupy the lowest-energy (σ) bonding orbital, thereby holding all three atoms together.

Hydrogen can lose its electron to form H^+, accept an electron to form H^-, share its electron, hydrogen bond, or form a three-center bond.

Synthesis, Reactions, and Compounds of Hydrogen

The first known preparation of elemental hydrogen was in 1671, when Robert Boyle dissolved iron in dilute acid and obtained a colorless, odorless, gaseous product. Hydrogen was finally identified as an element in 1766, when Henry Cavendish showed that water was the sole product of the reaction of the gas with oxygen. The explosive properties of mixtures of hydrogen with air were not discovered until early in the 18th century; they partially caused the spectacular explosion of the hydrogen-filled dirigible Hindenburg in 1937 (Figure 22.2.4). Due to its extremely low molecular mass, hydrogen gas is difficult to condense to a liquid (boiling point = 20.3 K), and solid hydrogen has one of the lowest melting points known (13.8 K).

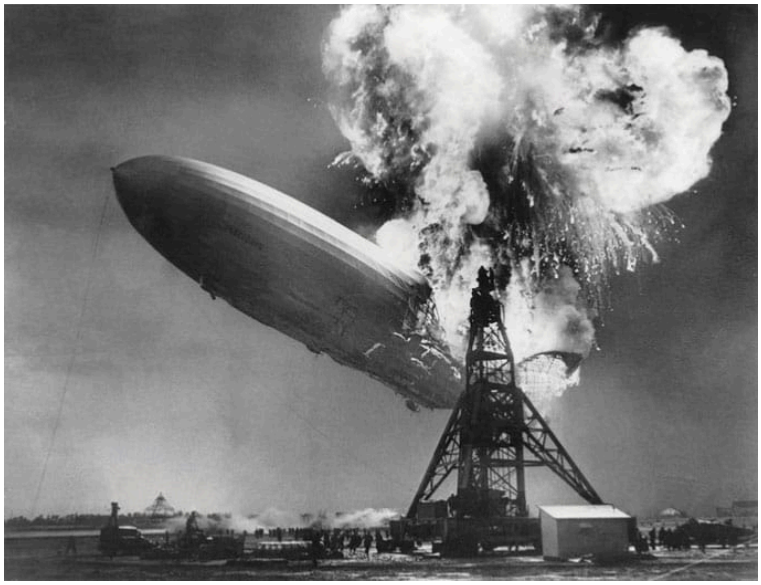


Figure 22.2.4: The Explosive Properties of Hydrogen. When mixed with air and ignited by a spark, hydrogen gas can explode. The photograph shows the German dirigible Hindenburg on fire at Lakehurst, New Jersey, in 1937, after its hydrogen compartment was accidentally ignited as a consequence of an electrical discharge that caused the dirigible's flammable skin to catch fire.

The most common way to produce small amounts of highly pure hydrogen gas in the laboratory was discovered by Boyle: reacting an active metal (M), such as iron, magnesium, or zinc, with dilute acid:

$$M_{(s)} + 2H^+_{(aq)} \rightarrow H_{2(g)} + M^{2+}_{(aq)} \tag{22.2.1}$$

Hydrogen gas can also be generated by reacting metals such as aluminum or zinc with a strong base:

$$\mathrm{Al(s) + OH^-(aq) + 3H_2O(l) \rightarrow \frac{3}{2}H_2(g) + [Al(OH)_4]^-(aq)} \tag{22.2.2}$$

Solid commercial drain cleaners such as Drano use this reaction to generate gas bubbles that help break up clogs in a drainpipe. Hydrogen gas is also produced by reacting ionic hydrides with water. Because ionic hydrides are expensive, however, this reaction is generally used for only specialized purposes, such as producing HD gas by reacting a hydride with D_2O:

$$MH_{(s)} + D_2O(l) \rightarrow HD_{(g)} + M^+(aq) + OD^-_{(aq)} \tag{22.2.3}$$

On an industrial scale, H_2 is produced from methane by means of catalytic steam reforming, a method used to convert hydrocarbons to a mixture of CO and H_2 known as synthesis gas, or syngas. The process is carried out at elevated temperatures (800°C) in the presence of a nickel catalyst:

$$\mathrm{CH_4(g) + H_2O(g) \xrightarrow{Ni} CO(g) + 3H_2(g)} \tag{22.2.4}$$

Most of the elements in the periodic table form binary compounds with hydrogen, which are collectively referred to as hydrides. Binary hydrides in turn can be classified in one of three ways, each with its own characteristic properties. Covalent hydrides contain hydrogen bonded to another atom via a covalent bond or a polar covalent bond. Covalent hydrides are usually molecular substances that are relatively volatile and have low melting points. Ionic hydrides contain the hydride ion as the anion with cations derived from electropositive metals. Like most ionic compounds, they are typically nonvolatile solids that contain three-dimensional lattices of cations and anions. Unlike most ionic compounds, however, they often decompose to H_2(g) and the parent metal after heating. Metallic hydrides are formed by hydrogen and less electropositive metals such as the transition metals. The properties of metallic hydrides are usually similar to those of the parent metal. Consequently, metallic hydrides are best viewed as metals that contain many hydrogen atoms present as interstitial impurities.

> Covalent hydrides are relatively volatile and have low melting points; ionic hydrides are generally nonvolatile solids in a lattice framework.

Summary and Key Takeaway

Hydrogen can lose an electron to form a proton, gain an electron to form a hydride ion, or form a covalent bond or polar covalent electron-pair bond. The three isotopes of hydrogen—protium (^{1}H or H), deuterium (^{2}H or D), and tritium (^{3}H or T)—have different physical properties. Deuterium and tritium can be used as tracers, substances that enable biochemists to follow the path of a molecule through an organism or a cell. Hydrogen can form compounds that contain a proton (H^+), a hydride ion (H^-), an electron-pair bond to H, a hydrogen bond, or a three-center bond (or electron-deficient bond), in which two electrons are shared between three atoms. Hydrogen gas can be generated by reacting an active metal with dilute acid, reacting Al or Zn with a strong base, or industrially by catalytic steam reforming, which produces synthesis gas, or syngas.

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22.3: Group 18- Noble Gases

Learning Objectives

- To understand the trends in properties and reactivity of the group 18 elements: the noble gases.

The noble gases were all isolated for the first time within a period of only five years at the end of the 19th century. Their very existence was not suspected until the 18th century, when early work on the composition of air suggested that it contained small amounts of gases in addition to oxygen, nitrogen, carbon dioxide, and water vapor. Helium was the first of the noble gases to be identified, when the existence of this previously unknown element on the sun was demonstrated by new spectral lines seen during a solar eclipse in 1868. Actual samples of helium were not obtained until almost 30 years later, however. In the 1890s, the English physicist J. W. Strutt (Lord Rayleigh) carefully measured the density of the gas that remained after he had removed all O_2, CO_2, and water vapor from air and showed that this residual gas was slightly denser than pure N_2 obtained by the thermal decomposition of ammonium nitrite. In 1894, he and the Scottish chemist William Ramsay announced the isolation of a new "substance" (not necessarily a new element) from the residual nitrogen gas. Because they could not force this substance to decompose or react with anything, they named it argon (Ar), from the Greek argos, meaning "lazy." Because the measured molar mass of argon was 39.9 g/mol, Ramsay speculated that it was a member of a new group of elements located on the right side of the periodic table between the halogens and the alkali metals. He also suggested that these elements should have a preferred valence of 0, intermediate between the +1 of the alkali metals and the –1 of the halogens.

J. W. Strutt (Lord Rayleigh) (1842–1919)

Lord Rayleigh was one of the few members of British higher nobility to be recognized as an outstanding scientist. Throughout his youth, his education was repeatedly interrupted by his frail health, and he was not expected to reach maturity. In 1861 he entered Trinity College, Cambridge, where he excelled at mathematics. A severe attack of rheumatic fever took him abroad, but in 1873 he succeeded to the barony and was compelled to devote his time to the management of his estates. After leaving the entire management to his younger brother, Lord Rayleigh was able to devote his time to science. He was a recipient of honorary science and law degrees from Cambridge University.

Sir William Ramsay (1852–1916)

Born and educated in Glasgow, Scotland, Ramsay was expected to study for the Calvanist ministry. Instead, he became interested in chemistry while reading about the manufacture of gunpowder. Ramsay earned his PhD in organic chemistry at the University of Tübingen in Germany in 1872. When he returned to England, his interests turned first to physical chemistry and then to inorganic chemistry. He is best known for his work on the oxides of nitrogen and for the discovery of the noble gases with Lord Rayleigh.

In 1895, Ramsey was able to obtain a terrestrial sample of helium for the first time. Then, in a single year (1898), he discovered the next three noble gases: krypton (Kr), from the Greek kryptos, meaning "hidden," was identified by its orange and green emission lines; neon (Ne), from the Greek neos, meaning "new," had bright red emission lines; and xenon (Xe), from the Greek xenos, meaning "strange," had deep blue emission lines. The last noble gas was discovered in 1900 by the German chemist Friedrich Dorn, who was investigating radioactivity in the air around the newly discovered radioactive elements radium and polonium. The element was named radon (Rn), and Ramsay succeeded in obtaining enough radon in 1908 to measure its density (and thus its atomic mass). For their discovery of the noble gases, Rayleigh was awarded the Nobel Prize in Physics and Ramsay the Nobel Prize in Chemistry in 1904. Because helium has the lowest boiling point of any substance known (4.2 K), it is used primarily as a cryogenic liquid. Helium and argon are both much less soluble in water (and therefore in blood) than N_2, so scuba divers often use gas mixtures that contain these gases, rather than N_2, to minimize the likelihood of the "bends," the painful and potentially fatal formation of bubbles of $N_2(g)$ that can occur when a diver returns to the surface too rapidly.

Preparation and General Properties of the Group 18 Elements

Fractional distillation of liquid air is the only source of all the noble gases except helium. Although helium is the second most abundant element in the universe (after hydrogen), the helium originally present in Earth's atmosphere was lost into space long ago because of its low molecular mass and resulting high mean velocity. Natural gas often contains relatively high concentrations of helium (up to 7%), however, and it is the only practical terrestrial source.

The elements of group 18 all have closed-shell valence electron configurations, either ns^2np^6 or $1s^2$ for He. Consistent with periodic trends in atomic properties, these elements have high ionization energies that decrease smoothly down the group. From their electron affinities, the data in Table 22.3.1 indicate that the noble gases are unlikely to form compounds in negative oxidation states. A potent oxidant is needed to oxidize noble gases and form compounds in positive oxidation states. Like the heavier halogens, xenon and perhaps krypton should form covalent compounds with F, O, and possibly Cl, in which they have even formal oxidation states (+2, +4, +6, and possibly +8). These predictions actually summarize the chemistry observed for these elements.

Table 22.3.1: Selected Properties of the Group 18 Elements

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
atomic symbol	He	Ne	Ar	Kr	Xe	Rn
atomic number	2	10	18	36	54	86
atomic mass (amu)	4.00	20.18	39.95	83.80	131.29	222
valence electron configuration*	$1s^2$	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$
triple point/boiling point (°C)	—/–269†	–249 (at 43 kPa)/–246	–189 (at 69 kPa)/–189	–157/–153	–112 (at 81.6 kPa)/–108	–71/–62
density (g/L) at 25°C	0.16	0.83	1.63	3.43	5.37	9.07
atomic radius (pm)	31	38	71	88	108	120
first ionization energy (kJ/mol)	2372	2081	1521	1351	1170	1037
normal oxidation state(s)	0	0	0	0 (+2)	0 (+2, +4, +6, +8)	0 (+2)
electron affinity (kJ/mol)	> 0	> 0	> 0	> 0	> 0	> 0
electronegativity	—	—	—	—	2.6	—
product of reaction with O_2	none	none	none	none	not directly with oxygen, but XeO_3 can be formed by Equation 22.3.5.	none
type of oxide	—	—	—	—	acidic	—
product of reaction with N_2	none	none	none	none	none	none
product of reaction with X_2	none	none	none	KrF_2	XeF_2, XeF_4, XeF_6	RnF_2
product of reaction with H_2	none	none	none	none	none	none

***The configuration shown does not include filled d and f subshells. †This is the normal boiling point of He. Solid He does not exist at 1 atm pressure, so no melting point can be given.**

Reactions and Compounds of the Noble Gases

For many years, it was thought that the only compounds the noble gases could form were clathrates. Clathrates are solid compounds in which a gas, the guest, occupies holes in a lattice formed by a less volatile, chemically dissimilar substance, the host (Figure 22.3.1).

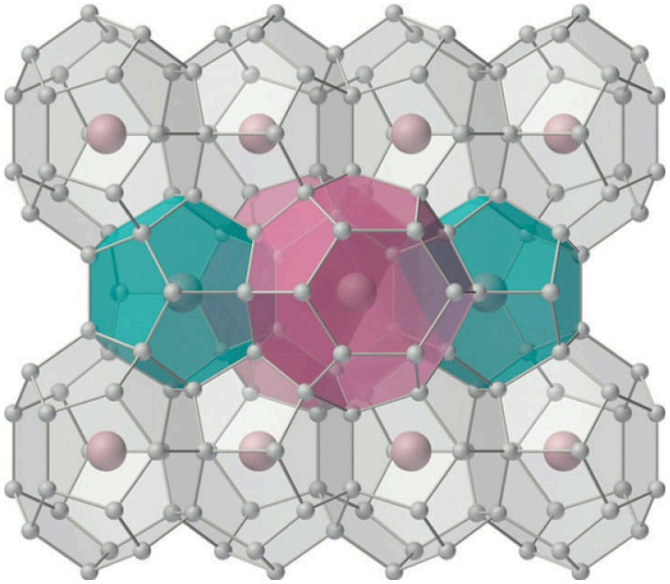


Figure 22.3.1: The Structure of Xenon Hydrate, a Clathrate. Small gaseous atoms or molecules such as Xe or CH_4 can occupy cavities in a lattice of hydrogen-bonded water molecules to produce a stable structure with a fixed stoichiometry (in this case, $Xe{\cdot}5.75H_2O$). (The hydrogen atoms of the water molecules have been omitted for clarity.) Warming the solid hydrate or decreasing the pressure of the gas causes it to collapse, with the evolution of gas and the formation of liquid water.

Because clathrate formation does not involve the formation of chemical bonds between the guest (Xe) and the host molecules (H_2O, in the case of xenon hydrate), the guest molecules are immediately released when the clathrate is melted or dissolved.

Methane Clathrates

In addition to the noble gases, many other species form stable clathrates. One of the most interesting is methane hydrate, large deposits of which occur naturally at the bottom of the oceans. It is estimated that the amount of methane in such deposits could have a major impact on the world's energy needs later in this century.



Figure 22.3.2: “Burning snowballs.” Like xenon, methane (CH_4) forms a crystalline clathrate with water: methane hydrate. When the solid is warmed, methane is released and can be ignited to give what appears to be burning snow. (left) Structure of a gas hydrate (methane clathrate) block embedded in the sediment of hydrate ridge, off Oregon, USA (CC-SA-BY-3.0 Wusel007) (middle) A ball-and-stick model of methane hydrate showing the central methane molecule surrounded by a "cage" of water molecules. Other hydrocarbon molecules such as pentane and ethane can occupy the central position in this structure. (United States Department of Energy image). (Right): A burning specimen of methane hydrate ice (United States Geological Survey image).

The widely held belief in the intrinsic lack of reactivity of the noble gases was challenged when Neil Bartlett, a British professor of chemistry at the University of British Columbia, showed that PtF_6, a compound used in the Manhattan Project, could oxidize O_2. Because the ionization energy of xenon (1170 kJ/mol) is actually lower than that of O_2, Bartlett recognized that PtF_6 should also be able to oxidize xenon. When he mixed colorless xenon gas with deep red PtF_6 vapor, yellow-orange crystals immediately formed (Figure 22.3.3). Although Bartlett initially postulated that they were $\mathrm{Xe^{+}PtF_6{}^{-}}$, it is now generally agreed that the reaction also involves the transfer of a fluorine atom to xenon to give the $\mathrm{XeF^{+}}$ ion:

$$\mathrm{Xe\,(g) + PtF_6\,(g) \longrightarrow [XeF^{+}][PtF_5{}^{-}]\,(s)} \tag{22.3.1}$$

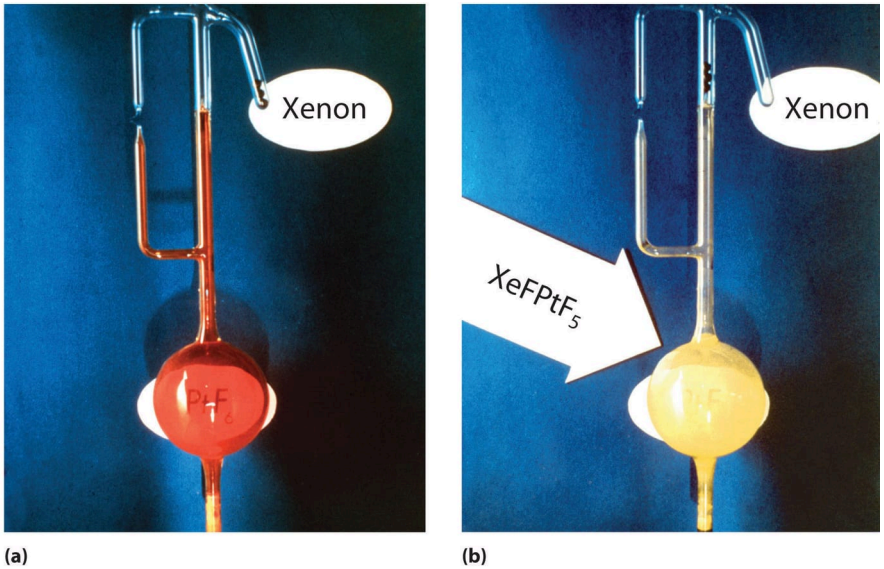


Figure 22.3.3: The Synthesis of the First Chemical Compound of Xenon. (a) An apparatus containing platinum hexafluoride, the red vapor at the bottom left, and xenon, the colorless gas in the small tube at the upper right. (b) When the glass seal separating the two gases is broken and the gases are allowed to mix, a bright yellow solid is formed, which is best described as $XeF^{+}PtF_5{}^{-}$.

Subsequent work showed that xenon reacts directly with fluorine under relatively mild conditions to give XeF_2, XeF_4, or XeF_6, depending on conditions; one such reaction is as follows:

$$\mathrm{Xe\,(g) + 2\,F_2\,(g) \longrightarrow XeF_4\,(s)} \tag{22.3.2}$$

The ionization energies of helium, neon, and argon are so high (Table 22.3.1) that no stable compounds of these elements are known. The ionization energies of krypton and xenon are lower but still very high; consequently only highly electronegative elements (F, O, and Cl) can form stable compounds with xenon and krypton without being oxidized themselves. Xenon reacts directly with only two elements: F_2 and Cl_2. Although $\mathrm{XeCl_2}$ and $\mathrm{KrF_2}$ can be prepared directly from the elements, they are substantially less stable than the xenon fluorides.

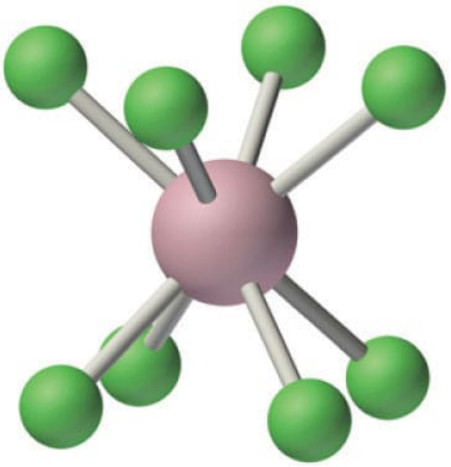
The ionization energies of helium, neon, and argon are so high that no stable compounds of these elements are known.

Because halides of the noble gases are powerful oxidants and fluorinating agents, they decompose rapidly after contact with trace amounts of water, and they react violently with organic compounds or other reductants. The xenon fluorides are also Lewis acids; they react with the fluoride ion, the only Lewis base that is not oxidized immediately on contact, to form anionic complexes. For example, reacting cesium fluoride with XeF_6 produces $CsXeF_7$, which gives Cs_2XeF_8 when heated:

$$\mathrm{XeF_6\,(s) + CsF\,(s) \longrightarrow CsXeF_7\,(s)} \tag{22.3.3}$$

$$\mathrm{2\,CsXeF_7\,(s) \xrightarrow{\Delta} Cs_2XeF_8\,(s) + XeF_6\,(g)} \tag{22.3.4}$$

The $\mathrm{XeF_8}^{2-}$ ion contains eight-coordinate xenon and has the square antiprismatic structure, which is essentially identical to that of the IF_8^- ion. Cs_2XeF_8 is surprisingly stable for a polyatomic ion that contains xenon in the +6 oxidation state, decomposing only at temperatures greater than 300°C. Major factors in the stability of Cs_2XeF_8 are almost certainly the formation of a stable ionic lattice and the **high coordination number** of xenon, which protects the central atom from attack by other species. (Recall from that this latter effect is responsible for the extreme stability of SF_6.)



For a previously “inert” gas, xenon has a surprisingly high affinity for oxygen, presumably because of π bonding between O and Xe. Consequently, xenon forms an extensive series of oxides and oxoanion salts. For example, hydrolysis of either XeF_4 or XeF_6 produces XeO_3, an explosive white solid:

$$\mathrm{XeF_6\,(aq) + 3\,H_2O\,(l) \longrightarrow XeO_3\,(aq) + 6\,HF\,(aq)} \tag{22.3.5}$$

Treating a solution of XeO_3 with ozone, a strong oxidant, results in further oxidation of xenon to give either XeO_4, a colorless, explosive gas, or the surprisingly stable perxenate ion (XeO_6^{4-}), both of which contain xenon in its highest possible oxidation state (+8). The chemistry of the xenon halides and oxides is best understood by analogy to the corresponding compounds of iodine. For example, XeO_3 is isoelectronic with the iodate ion (IO_3^-), and XeF_8^{2-} is isoelectronic with the IF_8^- ion.

Xenon has a high affinity for both fluorine and oxygen.

Because the ionization energy of radon is less than that of xenon, in principle radon should be able to form an even greater variety of chemical compounds than xenon. Unfortunately, however, radon is so radioactive that its chemistry has not been extensively explored.

Example 22.3.1

On a virtual planet similar to Earth, at least one isotope of radon is not radioactive. A scientist explored its chemistry and presented her major conclusions in a trailblazing paper on radon compounds, focusing on the kinds of compounds formed and their stoichiometries. Based on periodic trends, how did she summarize the chemistry of radon?

Given: nonradioactive isotope of radon

Asked for: summary of its chemistry

Strategy:

Based on the position of radon in the periodic table and periodic trends in atomic properties, thermodynamics, and kinetics, predict the most likely reactions and compounds of radon.

Solution

We expect radon to be significantly easier to oxidize than xenon. Based on its position in the periodic table, however, we also expect its bonds to other atoms to be weaker than those formed by xenon. Radon should be more difficult to oxidize to its highest possible oxidation state (+8) than xenon because of the inert-pair effect. Consequently, radon should form an extensive series of fluorides, including RnF_2, RnF_4, RnF_6, and possibly RnF_8 (due to its large radius). The ion RnF_8^{2-} should also exist. We expect radon to form a series of oxides similar to those of xenon, including RnO_3 and possibly RnO_4. The biggest surprise in radon chemistry is likely to be the existence of stable chlorides, such as $RnCl_2$ and possibly even $RnCl_4$.

Exercise 22.3.1

Predict the stoichiometry of the product formed by reacting XeF_6 with a 1:1 stoichiometric amount of KF and propose a reasonable structure for the anion.

Answer available at the end of this section.

Summary

The noble gases are characterized by their high ionization energies and low electron affinities. Potent oxidants are needed to oxidize the noble gases to form compounds in positive oxidation states. The noble gases have a closed-shell valence electron configuration. The ionization energies of the noble gases decrease with increasing atomic number. Only highly electronegative elements can form stable compounds with the noble gases in positive oxidation states without being oxidized themselves. Xenon has a high affinity for both fluorine and oxygen, which form stable compounds that contain xenon in even oxidation states up to +8.

Contributors and Attributions

- ◦ Anonymous

Answers

Exercise 22.3.1

$KXeF_7$; the xenon atom in XeF_7^- has 16 valence electrons, which according to the valence-shell electron-pair repulsion model could give either a square antiprismatic structure with one fluorine atom missing or a pentagonal bipyramid if the $5s^2$ electrons behave like an inert pair that does not participate in bonding.

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22.4: Group 17- The Halogens

Learning Objectives

- To understand the trends in properties and reactivity of the group 18 elements: the noble gases.

The noble gases were all isolated for the first time within a period of only five years at the end of the 19th century. Their very existence was not suspected until the 18th century, when early work on the composition of air suggested that it contained small amounts of gases in addition to oxygen, nitrogen, carbon dioxide, and water vapor. Helium was the first of the noble gases to be identified, when the existence of this previously unknown element on the sun was demonstrated by new spectral lines seen during a solar eclipse in 1868. Actual samples of helium were not obtained until almost 30 years later, however. In the 1890s, the English physicist J. W. Strutt (Lord Rayleigh) carefully measured the density of the gas that remained after he had removed all O_2, CO_2, and water vapor from air and showed that this residual gas was slightly denser than pure N_2 obtained by the thermal decomposition of ammonium nitrite. In 1894, he and the Scottish chemist William Ramsay announced the isolation of a new "substance" (not necessarily a new element) from the residual nitrogen gas. Because they could not force this substance to decompose or react with anything, they named it argon (Ar), from the Greek argos, meaning "lazy." Because the measured molar mass of argon was 39.9 g/mol, Ramsay speculated that it was a member of a new group of elements located on the right side of the periodic table between the halogens and the alkali metals. He also suggested that these elements should have a preferred valence of 0, intermediate between the +1 of the alkali metals and the –1 of the halogens.

J. W. Strutt (Lord Rayleigh) (1842–1919)

Lord Rayleigh was one of the few members of British higher nobility to be recognized as an outstanding scientist. Throughout his youth, his education was repeatedly interrupted by his frail health, and he was not expected to reach maturity. In 1861 he entered Trinity College, Cambridge, where he excelled at mathematics. A severe attack of rheumatic fever took him abroad, but in 1873 he succeeded to the barony and was compelled to devote his time to the management of his estates. After leaving the entire management to his younger brother, Lord Rayleigh was able to devote his time to science. He was a recipient of honorary science and law degrees from Cambridge University.

Sir William Ramsay (1852–1916)

Born and educated in Glasgow, Scotland, Ramsay was expected to study for the Calvanist ministry. Instead, he became interested in chemistry while reading about the manufacture of gunpowder. Ramsay earned his PhD in organic chemistry at the University of Tübingen in Germany in 1872. When he returned to England, his interests turned first to physical chemistry and then to inorganic chemistry. He is best known for his work on the oxides of nitrogen and for the discovery of the noble gases with Lord Rayleigh.

In 1895, Ramsey was able to obtain a terrestrial sample of helium for the first time. Then, in a single year (1898), he discovered the next three noble gases: krypton (Kr), from the Greek kryptos, meaning "hidden," was identified by its orange and green emission lines; neon (Ne), from the Greek neos, meaning "new," had bright red emission lines; and xenon (Xe), from the Greek xenos, meaning "strange," had deep blue emission lines. The last noble gas was discovered in 1900 by the German chemist Friedrich Dorn, who was investigating radioactivity in the air around the newly discovered radioactive elements radium and polonium. The element was named radon (Rn), and Ramsay succeeded in obtaining enough radon in 1908 to measure its density (and thus its atomic mass). For their discovery of the noble gases, Rayleigh was awarded the Nobel Prize in Physics and Ramsay the Nobel Prize in Chemistry in 1904. Because helium has the lowest boiling point of any substance known (4.2 K), it is used primarily as a cryogenic liquid. Helium and argon are both much less soluble in water (and therefore in blood) than N_2, so scuba divers often use gas mixtures that contain these gases, rather than N_2, to minimize the likelihood of the "bends," the painful and potentially fatal formation of bubbles of $N_2(g)$ that can occur when a diver returns to the surface too rapidly.

Preparation and General Properties of the Group 18 Elements

Fractional distillation of liquid air is the only source of all the noble gases except helium. Although helium is the second most abundant element in the universe (after hydrogen), the helium originally present in Earth's atmosphere was lost into space long ago because of its low molecular mass and resulting high mean velocity. Natural gas often contains relatively high concentrations of helium (up to 7%), however, and it is the only practical terrestrial source.

The elements of group 18 all have closed-shell valence electron configurations, either ns^2np^6 or $1s^2$ for He. Consistent with periodic trends in atomic properties, these elements have high ionization energies that decrease smoothly down the group. From their electron affinities, the data in Table 22.4.1 indicate that the noble gases are unlikely to form compounds in negative oxidation states. A potent oxidant is needed to oxidize noble gases and form compounds in positive oxidation states. Like the heavier halogens, xenon and perhaps krypton should form covalent compounds with F, O, and possibly Cl, in which they have even formal oxidation states (+2, +4, +6, and possibly +8). These predictions actually summarize the chemistry observed for these elements.

Table 22.4.1: Selected Properties of the Group 18 Elements

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
atomic symbol	He	Ne	Ar	Kr	Xe	Rn
atomic number	2	10	18	36	54	86
atomic mass (amu)	4.00	20.18	39.95	83.80	131.29	222
valence electron configuration*	$1s^2$	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$
triple point/boiling point (°C)	—/−269†	−249 (at 43 kPa)/−246	−189 (at 69 kPa)/−189	−157/−153	−112 (at 81.6 kPa)/−108	−71/−62
density (g/L) at 25°C	0.16	0.83	1.63	3.43	5.37	9.07
atomic radius (pm)	31	38	71	88	108	120
first ionization energy (kJ/mol)	2372	2081	1521	1351	1170	1037
normal oxidation state(s)	0	0	0	0 (+2)	0 (+2, +4, +6, +8)	0 (+2)
electron affinity (kJ/mol)	> 0	> 0	> 0	> 0	> 0	> 0
electronegativity	—	—	—	—	2.6	—
product of reaction with O_2	none	none	none	none	not directly with oxygen, but XeO_3 can be formed by Equation 22.4.5.	none
type of oxide	—	—	—	—	acidic	—
product of reaction with N_2	none	none	none	none	none	none
product of reaction with X_2	none	none	none	KrF_2	XeF_2, XeF_4, XeF_6	RnF_2
product of reaction with H_2	none	none	none	none	none	none

***The configuration shown does not include filled d and f subshells. †This is the normal boiling point of He. Solid He does not exist at 1 atm pressure, so no melting point can be given.**

Reactions and Compounds of the Noble Gases

For many years, it was thought that the only compounds the noble gases could form were clathrates. Clathrates are solid compounds in which a gas, the guest, occupies holes in a lattice formed by a less volatile, chemically dissimilar substance, the host (Figure 22.4.1).

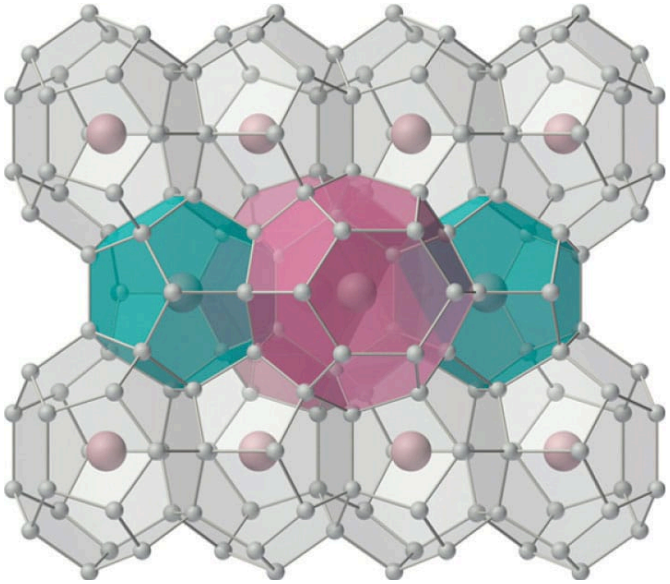


Figure 22.4.1: The Structure of Xenon Hydrate, a Clathrate. Small gaseous atoms or molecules such as Xe or CH_4 can occupy cavities in a lattice of hydrogen-bonded water molecules to produce a stable structure with a fixed stoichiometry (in this case, $Xe{\cdot}5.75H_2O$). (The hydrogen atoms of the water molecules have been omitted for clarity.) Warming the solid hydrate or decreasing the pressure of the gas causes it to collapse, with the evolution of gas and the formation of liquid water.

Because clathrate formation does not involve the formation of chemical bonds between the guest (Xe) and the host molecules (H_2O, in the case of xenon hydrate), the guest molecules are immediately released when the clathrate is melted or dissolved.

Methane Clathrates

In addition to the noble gases, many other species form stable clathrates. One of the most interesting is methane hydrate, large deposits of which occur naturally at the bottom of the oceans. It is estimated that the amount of methane in such deposits could have a major impact on the world's energy needs later in this century.



Figure 22.4.2: “Burning snowballs.” Like xenon, methane (CH_4) forms a crystalline clathrate with water: methane hydrate. When the solid is warmed, methane is released and can be ignited to give what appears to be burning snow. (left) Structure of a gas hydrate (methane clathrate) block embedded in the sediment of hydrate ridge, off Oregon, USA (CC-SA-BY-3.0 Wusel007) (middle) A ball-and-stick model of methane hydrate showing the central methane molecule surrounded by a "cage" of water molecules. Other hydrocarbon molecules such as pentane and ethane can occupy the central position in this structure. (United States Department of Energy image). (Right): A burning specimen of methane hydrate ice (United States Geological Survey image).

The widely held belief in the intrinsic lack of reactivity of the noble gases was challenged when Neil Bartlett, a British professor of chemistry at the University of British Columbia, showed that PtF_6, a compound used in the Manhattan Project, could oxidize O_2. Because the ionization energy of xenon (1170 kJ/mol) is actually lower than that of O_2, Bartlett recognized that PtF_6 should also be able to oxidize xenon. When he mixed colorless xenon gas with deep red PtF_6 vapor, yellow-orange crystals immediately formed (Figure 22.4.3). Although Bartlett initially postulated that they were $\mathrm{Xe^{+}PtF_6{}^{-}}$, it is now generally agreed that the reaction also involves the transfer of a fluorine atom to xenon to give the $\mathrm{XeF^{+}}$ ion:

$$\mathrm{Xe\,(g) + PtF_6\,(g) \longrightarrow [XeF^{+}][PtF_5{}^{-}]\,(s)} \tag{22.4.1}$$

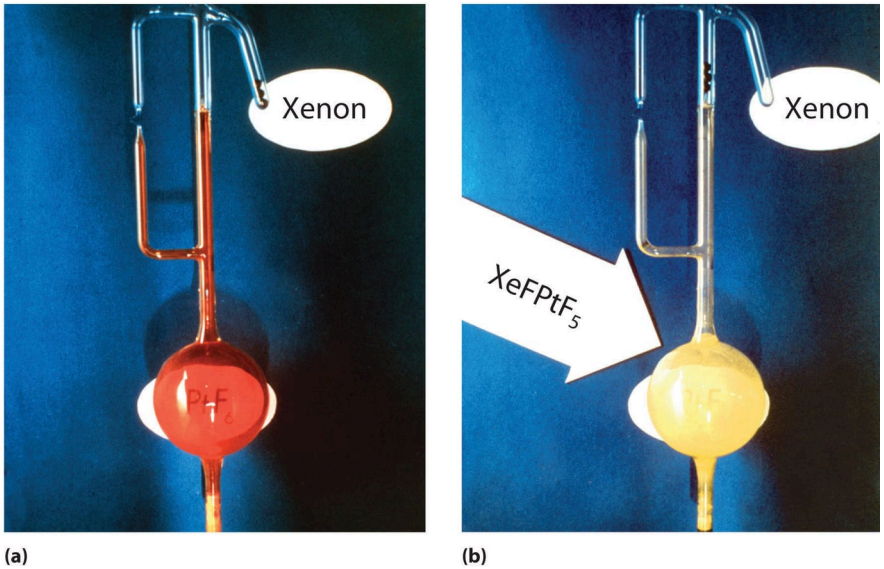


Figure 22.4.3: The Synthesis of the First Chemical Compound of Xenon. (a) An apparatus containing platinum hexafluoride, the red vapor at the bottom left, and xenon, the colorless gas in the small tube at the upper right. (b) When the glass seal separating the two gases is broken and the gases are allowed to mix, a bright yellow solid is formed, which is best described as $XeF^{+}PtF_5{}^{-}$.

Subsequent work showed that xenon reacts directly with fluorine under relatively mild conditions to give XeF_2, XeF_4, or XeF_6, depending on conditions; one such reaction is as follows:

$$\mathrm{Xe\,(g) + 2\,F_2\,(g) \longrightarrow XeF_4\,(s)} \tag{22.4.2}$$

The ionization energies of helium, neon, and argon are so high (Table 22.4.1) that no stable compounds of these elements are known. The ionization energies of krypton and xenon are lower but still very high; consequently only highly electronegative elements (F, O, and Cl) can form stable compounds with xenon and krypton without being oxidized themselves. Xenon reacts directly with only two elements: F_2 and Cl_2. Although $\mathrm{XeCl_2}$ and $\mathrm{KrF_2}$ can be prepared directly from the elements, they are substantially less stable than the xenon fluorides.

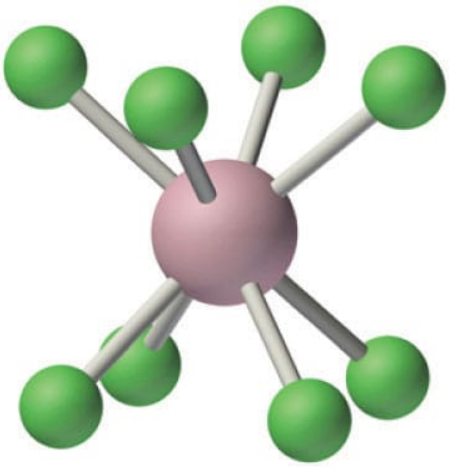
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$$\mathrm{XeF_6\,(s) + CsF\,(s) \longrightarrow CsXeF_7\,(s)} \tag{22.4.3}$$

$$\mathrm{2\,CsXeF_7\,(s) \xrightarrow{\Delta} Cs_2XeF_8\,(s) + XeF_6\,(g)} \tag{22.4.4}$$

The $\mathrm{XeF_8}^{2-}$ ion contains eight-coordinate xenon and has the square antiprismatic structure, which is essentially identical to that of the IF_8^- ion. Cs_2XeF_8 is surprisingly stable for a polyatomic ion that contains xenon in the +6 oxidation state, decomposing only at temperatures greater than 300°C. Major factors in the stability of Cs_2XeF_8 are almost certainly the formation of a stable ionic lattice and the **high coordination number** of xenon, which protects the central atom from attack by other species. (Recall from that this latter effect is responsible for the extreme stability of SF_6.)



For a previously “inert” gas, xenon has a surprisingly high affinity for oxygen, presumably because of π bonding between O and Xe. Consequently, xenon forms an extensive series of oxides and oxoanion salts. For example, hydrolysis of either XeF_4 or XeF_6 produces XeO_3, an explosive white solid:

$$\mathrm{XeF_6\,(aq) + 3\,H_2O\,(l) \longrightarrow XeO_3\,(aq) + 6\,HF\,(aq)} \tag{22.4.5}$$

Treating a solution of XeO_3 with ozone, a strong oxidant, results in further oxidation of xenon to give either XeO_4, a colorless, explosive gas, or the surprisingly stable perxenate ion (XeO_6^{4-}), both of which contain xenon in its highest possible oxidation state (+8). The chemistry of the xenon halides and oxides is best understood by analogy to the corresponding compounds of iodine. For example, XeO_3 is isoelectronic with the iodate ion (IO_3^-), and XeF_8^{2-} is isoelectronic with the IF_8^- ion.

Xenon has a high affinity for both fluorine and oxygen.

Because the ionization energy of radon is less than that of xenon, in principle radon should be able to form an even greater variety of chemical compounds than xenon. Unfortunately, however, radon is so radioactive that its chemistry has not been extensively explored.

Example 22.4.1

On a virtual planet similar to Earth, at least one isotope of radon is not radioactive. A scientist explored its chemistry and presented her major conclusions in a trailblazing paper on radon compounds, focusing on the kinds of compounds formed and their stoichiometries. Based on periodic trends, how did she summarize the chemistry of radon?

Given: nonradioactive isotope of radon

Asked for: summary of its chemistry

Strategy:

Based on the position of radon in the periodic table and periodic trends in atomic properties, thermodynamics, and kinetics, predict the most likely reactions and compounds of radon.

Solution

We expect radon to be significantly easier to oxidize than xenon. Based on its position in the periodic table, however, we also expect its bonds to other atoms to be weaker than those formed by xenon. Radon should be more difficult to oxidize to its highest possible oxidation state (+8) than xenon because of the inert-pair effect. Consequently, radon should form an extensive series of fluorides, including RnF_2, RnF_4, RnF_6, and possibly RnF_8 (due to its large radius). The ion RnF_8^{2-} should also exist. We expect radon to form a series of oxides similar to those of xenon, including RnO_3 and possibly RnO_4. The biggest surprise in radon chemistry is likely to be the existence of stable chlorides, such as $RnCl_2$ and possibly even $RnCl_4$.

Exercise 22.4.1

Predict the stoichiometry of the product formed by reacting XeF_6 with a 1:1 stoichiometric amount of KF and propose a reasonable structure for the anion.

Answer available at the end of this section.

Summary

The noble gases are characterized by their high ionization energies and low electron affinities. Potent oxidants are needed to oxidize the noble gases to form compounds in positive oxidation states. The noble gases have a closed-shell valence electron configuration. The ionization energies of the noble gases decrease with increasing atomic number. Only highly electronegative elements can form stable compounds with the noble gases in positive oxidation states without being oxidized themselves. Xenon has a high affinity for both fluorine and oxygen, which form stable compounds that contain xenon in even oxidation states up to +8.

Contributors and Attributions

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Answers

Exercise 22.4.1

$KXeF_7$; the xenon atom in XeF_7^- has 16 valence electrons, which according to the valence-shell electron-pair repulsion model could give either a square antiprismatic structure with one fluorine atom missing or a pentagonal bipyramid if the $5s^2$ electrons behave like an inert pair that does not participate in bonding.

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22.5: Oxygen

Oxygen is an element that is widely known by the general public because of the large role it plays in sustaining life. Without oxygen, animals would be unable to breathe and would consequently die. Oxygen not only is important to supporting life, but also plays an important role in many other chemical reactions. Oxygen is the most common element in the earth's crust and makes up about 20% of the air we breathe. Historically the discovery of oxygen as an element essential for combustion stands at the heart of the phlogiston controversy (see below).

The Origin and History

Oxygen is found in the group 16 elements and is considered a chalcogen. Named from the Greek oxys + genes, "acid-former", oxygen was discovered in 1772 by Scheele and independently by Priestly in 1774. Oxygen was given its name by the French scientist, Antoine Lavoisier.

Scheele discovered oxygen through an experiment which involved burning manganese oxide. Scheele came to find that the hot manganese oxide produced a gas which he called "fire air". He also came to find that when this gas was able to come into contact with charcoal, it produced beautiful bright sparks. All of the other elements produced the same gas. Although Scheele discovered oxygen, he did not publish his work until three years after another chemist, Joseph Priestly, discovered oxygen. Joseph Priestly, an English chemist, repeated Scheele's experiment in 1774 using a slightly different setup. Priestly used a 12 in burning glass and aimed the sunlight directly towards the compound that he was testing, mercuric oxide. As a result, he was able to "discover better air" that was shown to expand a mouse's lifetime to four times as long and caused a flame to burn with higher intensity. Despite these experiments, both chemists were not able to pinpoint exactly what this element was. It was not until 1775 that Antoine Lavoisier, a French chemist, was able to recognize this unknown gas as an element.

Our atmosphere currently contains about 21% of free oxygen. Oxygen is produced in various ways. The process of photochemical dissociation in which water molecules are broken up by ultraviolet rays produces about 1-2% of our oxygen. Another process that produces oxygen is photosynthesis which is performed by plants and photosynthetic bacteria. Photosynthesis occurs through the following general reaction:

$$\mathrm{CO_2 + H_2O + h\nu \rightarrow organic\ compounds + O_2}$$

The Dangers of Phlogiston

Phlogiston theory is the outdated belief that a fire-like element called phlogiston is contained within combustible bodies and released during combustion. The name comes from the Ancient Greek φλογιστόν phlogistón (burning up), from φλόξ phlóx (flame). It was first stated in 1667 by Johann Joachim Becher, and then put together more formally by Georg Ernst Stahl. The theory attempted to explain burning processes such as combustion and rusting, which are now collectively known as oxidation.

Properties

- Element number: 8
- Atomic weight 15.9994
- Color: gas form- colorless, liquid- pale blue
- Melting point: 54.36K
- Boiling point: 90.2 K
- Density: .001429
- 21% of earth's atmosphere
- Third most abundant element in the universe
- Most abundant element in Earth's crust at 45.4%
- 3 Stable isotopes
- Ionization energy: 13.618 eV
- Oxygen is easily reduced and is a great oxidizing agent making it readily reactive with other elements

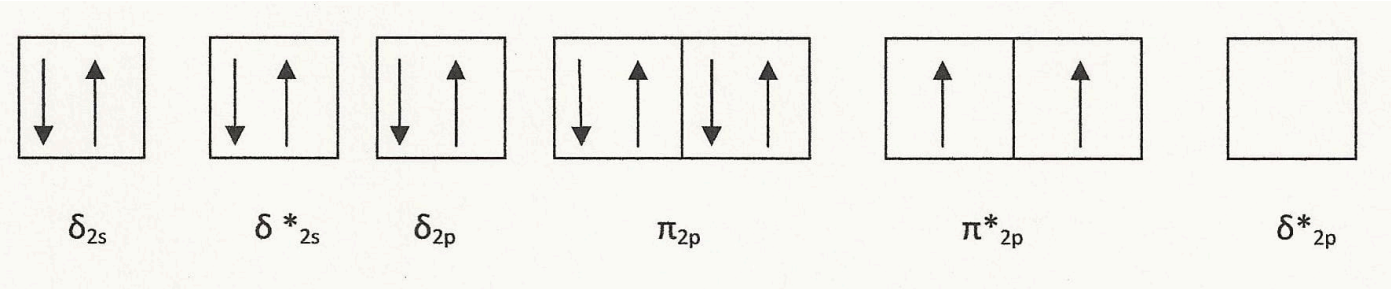
YouTube Video

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View this YouTube Video online

Magnetic Properties of Oxygen

Oxygen (O_2) is paramagnetic. An oxygen molecule has six valence electrons, so the O_2 molecule has 12 valence electrons with the electron configuration shown below:



As shown, there are two unpaired electrons, which causes O_2 to be paramagnetic. There are also eight valence electrons in the bonding orbitals and four in antibonding orbitals, which makes the bond order 2. This accounts for the double covalent bond that is present in O_2.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video $22.5.1$***:*** *A chemical demonstration of the paramagnetism of molecular oxygen, as shown by the attraction of liquid oxygen to magnets.*

As shown in Video $22.5.1$, since molecular oxygen (O_2) has unpaired electrons, it is paramagnetic and is attracted to the magnet. In contrast, molecular nitrogen (N_2) has no unpaired electrons and is not attracted to the magnet.

General Chemistry of Oxygen

Oxygen normally has an oxidation state of -2, but is capable of having oxidation states of -2, -1, -1/2, 0, +1, and +2. The oxidation states of oxides, peroxides and superoxides are as follows:

- Oxides: O^{-2} ,
- peroxides: O_2^{-2} ,
- superoxide: O_2^{-1}.

Oxygen does not react with itself, nitrogen, or water under normal conditions. Oxygen does, however, dissolve in water at 20 degrees Celsius and 1 atmosphere. Oxygen also does not normally react with bases or acids. Group 1 metals (alkaline metals) are very reactive with oxygen and must be stored away from oxygen in order to prevent them from becoming oxidized. The metals at the bottom of the group are more reactive than those at the top. The reactions of a few of these metals are explored in more detail below.

Lithium: Reacts with oxygen to form white lithium oxide in the reaction below.

$$4\,\mathrm{Li} + \mathrm{O_2} \rightarrow 2\,\mathrm{Li_2O} \tag{22.5.1}$$

Sodium: Reacts with oxygen to form a white mixture of sodium oxide and sodium peroxide. The reactions are shown below.

- Sodium oxide:

$$4\,\mathrm{Na} + \mathrm{O_2} \rightarrow 2\,\mathrm{Na_2O} \tag{22.5.2}$$

- Sodium peroxide:

$$2\,\mathrm{Na} + \mathrm{O_2} \rightarrow \mathrm{Na_2O_2} \tag{22.5.3}$$

Potassium: Reacts with oxygen to form a mixture of potassium peroxide and potassium superoxide. The reactions are shown below.

- Potassium peroxide:

$$2\,\mathrm{K} + \mathrm{O_2} \rightarrow 2\,\mathrm{K_2O_2} \tag{22.5.4}$$

- Potassium superoxide:

$$\mathrm{K} + \mathrm{O_2} \rightarrow \mathrm{KO_2} \tag{22.5.5}$$

Rubidium and Cesium: Both metals react to produce superoxides through the same process as that of the potassium superoxide reaction.

> The oxides of these metals form metal hydroxides when they react with water. These metal hydroxides make the solution basic or alkaline, hence the name alkaline metals.

Group 2 metals (alkaline earth metals) react with oxygen through the process of burning to form metal oxides but there are a few exceptions.

Beryllium is very difficult to burn because it has a layer of beryllium oxide on its surface which prevents further interaction with oxygen. Strontium and barium react with oxygen to form peroxides. The reaction of barium and oxygen is shown below, and the reaction with strontium would be the same.

$$\mathrm{Ba\,(s)} + \mathrm{O_2\,(g)} \rightarrow \mathrm{BaO_2\,(s)} \tag{22.5.6}$$

Group 13 reacts with oxygen in order to form oxides and hydroxides that are of the form X_2O_3 and $X(OH)_3$. The variable X represents the various group 13 elements. As you go down the group, the oxides and hydroxides get increasingly basic.

Group 14 elements react with oxygen to form oxides. The oxides formed at the top of the group are more acidic than those at the bottom of the group. Oxygen reacts with silicon and carbon to form silicon dioxide and carbon dioxide. Carbon is also able to react with oxygen to form carbon monoxide, which is slightly acidic. Germanium, tin, and lead react with oxygen to form monoxides and dioxides that are amphoteric, which means that they react with both acids and bases.

Group 15 elements react with oxygen to form oxides. The most important are listed below.

- Nitrogen: N_2O, NO, N_2O_3, N_2O_4, N_2O_5
- Phosphorus: P_4O_6, P_4O_8, P_2O_5
- Arsenic: As_2O_3, As_2O_5
- Antimony: Sb_2O_3, Sb_2O_5
- Bismuth: Bi_2O_3, Bi_2O_5

Group 16 elements react with oxygen to form various oxides. Some of the oxides are listed below.

- Sulfur: SO, SO_2, SO_3, S_2O_7
- Selenium: SeO_2, SeO_3
- Tellurium: TeO, TeO_2, TeO_3
- Polonium: PoO, PoO_2, PoO_3

Group 17 elements (halogens) fluorine, chlorine, bromine, and iodine react with oxygen to form oxides. Fluorine forms two oxides with oxygen: F_2O and F_2O_2. Both fluorine oxides are called oxygen fluorides because fluorine is the more electronegative element. One of the fluorine reactions is shown below.

$$\mathrm{O_2\,(g) + F_2\,(g)\ \rightarrow F_2O_2\,(g)} \tag{22.5.7}$$

Group 18: Some would assume that the Noble Gases would not react with oxygen. However, xenon does react with oxygen to form $\mathrm{XeO_3}$ and $\mathrm{XeO_4}$. The ionization energy of xenon is low enough for the electronegative oxygen atom to "steal away" electrons. Unfortunately, $\mathrm{XeO_3}$ is HIGHLY unstable, and it has been known to spontaneously detonate in a clean, dry environment.

Transition metals react with oxygen to form metal oxides. However, gold, silver, and platinum do not react with oxygen. A few reactions involving transition metals are shown below:

$$2Sn_{(s)} + O_{2(g)} \rightarrow 2SnO_{(s)} \tag{22.5.8}$$

$$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)} \tag{22.5.9}$$

$$4Al_{(s)} + 3O_{2(g)} \rightarrow 2Al_2O_{3(s)} \tag{22.5.10}$$

Reaction of Oxides

We will be discussing metal oxides of the form X_2O. The variable X represents any metal that is able to bond to oxygen to form an oxide.

- **Reaction with water:** The oxides react with water to form a metal hydroxide.

$$X_2O + H_2O \rightarrow 2XOH$$

- **Reaction with dilute acids:** The oxides react with dilute acids to form a salt and water.

$$X_2O + 2HCl \rightarrow 2XCl + H_2O$$

Reactions of Peroxides

The peroxides we will be discussing are of the form X_2O_2. The variable X represents any metal that can form a peroxide with oxygen.

Reaction with water: If the temperature of the reaction is kept constant despite the fact that the reaction is exothermic, then the reaction proceeds as follows:

$$X_2O_2 + 2H_2O \rightarrow 2XOH + H_2O_2$$

If the reaction is not carried out at a constant temperature, then the reaction of the peroxide and water will result in decomposition of the hydrogen peroxide that is produced into water and oxygen.

Reaction with dilute acid: This reaction is more exothermic than that with water. The heat produced causes the hydrogen peroxide to decompose to water and oxygen. The reaction is shown below.

$$X_2O_2 + 2HCl \rightarrow 2XCl + H_2O_2$$

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Reaction of Superoxides

The superoxides we will be talking about are of the form XO_2, with X representing any metal that forms a superoxide when reacting with oxygen.

Reaction with water: The superoxide and water react in a very exothermic reaction that is shown below. The heat that is produced in forming the hydrogen peroxide will cause the hydrogen peroxide to decompose to water and oxygen.

$$2XO_2 + 2H_2O \rightarrow 2XOH + H_2O_2 + O_2$$

Reaction with dilute acids: The superoxide and dilute acid react in a very exothermic reaction that is shown below. The heat produced will cause the hydrogen peroxide to decompose to water and oxygen.

$$2XO_2 + 2HCl \rightarrow 2XCl + H_2O_2 + O_2$$

Allotropes of Oxygen

There are two allotropes of oxygen; dioxygen (O_2) and trioxygen (O_3) which is called ozone. The reaction of converting dioxygen into ozone is very endothermic, causing it to occur rarely and only in the lower atmosphere. The reaction is shown below:

$$3O_{2(g)} \rightarrow 2O_{3(g)} \quad \Delta H^o = +285\ kJ$$

Ozone is unstable and quickly decomposes back to oxygen but is a great oxidizing agent.

Miscellaneous Reactions

Reaction with Alkanes: The most common reactions that involve alkanes occur with oxygen. Alkanes are able to burn and it is the process of oxidizing the hydrocarbons that makes them important as fuels. An example of an alkane reaction is the reaction of octane with oxygen as shown below.

$$C_8H_{18}(l) + 25/2\ O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)\ \Delta H_o = -5.48 \times 10^3\ kJ$$

Reaction with ammonia: Oxygen is able to react with ammonia to produce dinitrogen (N_2) and water (H_2O) through the reaction shown below.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Reaction with Nitrogen Oxide: Oxygen is able to react with nitrogen oxide in order to produce nitrogen dioxide through the reaction shown below.

$$NO + O_2 \rightarrow NO_2$$

Problems

1. Is oxygen reactive with noble gases?
2. Which transition metals does oxygen not react with?
3. What is produced when an oxide reacts with water?
4. Is oxygen reactive with alkali metals? Why are the alkali metals named that way?
5. If oxygen is reactive with alkali metals, are oxides, peroxides or superoxides produced?

Solutions

1. No, noble gases are unreactive with oxygen.
2. Oxygen is mostly unreactive with gold and platinum.
3. When an oxide reacts with water, a metal hydroxide is produced.
4. Oxygen is very reactive with alkali metals. Alkali metals are given the name alkali because the oxides of these metals react

with water to form a metal hydroxide that is basic or alkaline.
5. Lithium produces an oxide, sodium produces a peroxide, and potassium, cesium, and rubidium produce superoxides.

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22.6: The Other Group 16 Elements- S, Se, Te, and Po

Learning Objectives

- To understand the trends in properties and reactivity of the group 16 elements: the chalcogens.

The chalcogens are the first group in the p block to have no stable metallic elements. All isotopes of polonium (Po), the only metal in group 16, are radioactive, and only one element in the group, tellurium (Te), can even be described as a semimetal. As in groups 14 and 15, the lightest element of group 16, oxygen, is found in nature as the free element.

Of the group 16 elements, only sulfur was known in ancient times; the others were not discovered until the late 18th and 19th centuries. Sulfur is frequently found as yellow crystalline deposits of essentially pure S_8 in areas of intense volcanic activity or around hot springs. As early as the 15th century BC, sulfur was used as a fumigant in Homeric Greece because, when burned, it produces SO_2 fumes that are toxic to most organisms, including vermin hiding in the walls and under the floors of houses. Hence references to sulfur are common in ancient literature, frequently in the context of religious purification. In fact, the association of sulfur with the divine was so pervasive that the prefixes thio- (meaning “sulfur”) and theo- (meaning “god”) have the same root in ancient Greek. Though used primarily in the production of sulfuric acid, sulfur is also used to manufacture gunpowder and as a cross-linking agent for rubber, which enables rubber to hold its shape but retain its flexibility.

Group 16 is the first group in the p block with no stable metallic elements.

Oxygen was not discovered until 1771, when the Swedish pharmacist Carl Wilhelm Scheele found that heating compounds such as KNO_3, Ag_2CO_3, and HgO produced a colorless, odorless gas that supported combustion better than air. The results were not published immediately, however, so Scheele’s work remained unknown until 1777. Unfortunately, this was nearly two years after a paper by the English chemist Joseph Priestley had been published, describing the isolation of the same gas by using a magnifying glass to focus the sun’s rays on a sample of HgO. Oxygen is used primarily in the steel industry during the conversion of crude iron to steel using the Bessemer process. Another important industrial use of oxygen is in the production of TiO_2, which is commonly used as a white pigment in paints, paper, and plastics.



Figure 22.6.1: A crystalline sulfur deposit. This sulfur deposit is located around a volcanic vent in Kilauea Crater, Hawaii.

Tellurium was discovered accidentally in 1782 by the Austrian chemist Franz Joseph Müller von Reichenstein, the chief surveyor of mines in Transylvania who was also responsible for the analysis of ore samples. The silvery-white metal had the same density as antimony but very different properties. Because it was difficult to analyze, Müller called it metallum problematicum (meaning “difficult metal”). The name tellurium (from the Latin tellus, meaning “earth”) was coined by another Austrian chemist, Martin

Klaproth, who demonstrated in 1798 that Müller's "difficult metal" was actually a new element. Tellurium is used to color glass and ceramics, in the manufacture of blasting caps, and in thermoelectric devices.

Jöns Jakob Berzelius (1779–1848)

Berzelius was born into a well-educated Swedish family, but both parents died when he was young. He studied medicine at the University of Uppsala, where his experiments with electroshock therapy caused his interests to turn to electrochemistry. Berzelius devised the system of chemical notation that we use today. In addition, he discovered six elements (cerium, thorium, selenium, silicon, titanium, and zirconium).

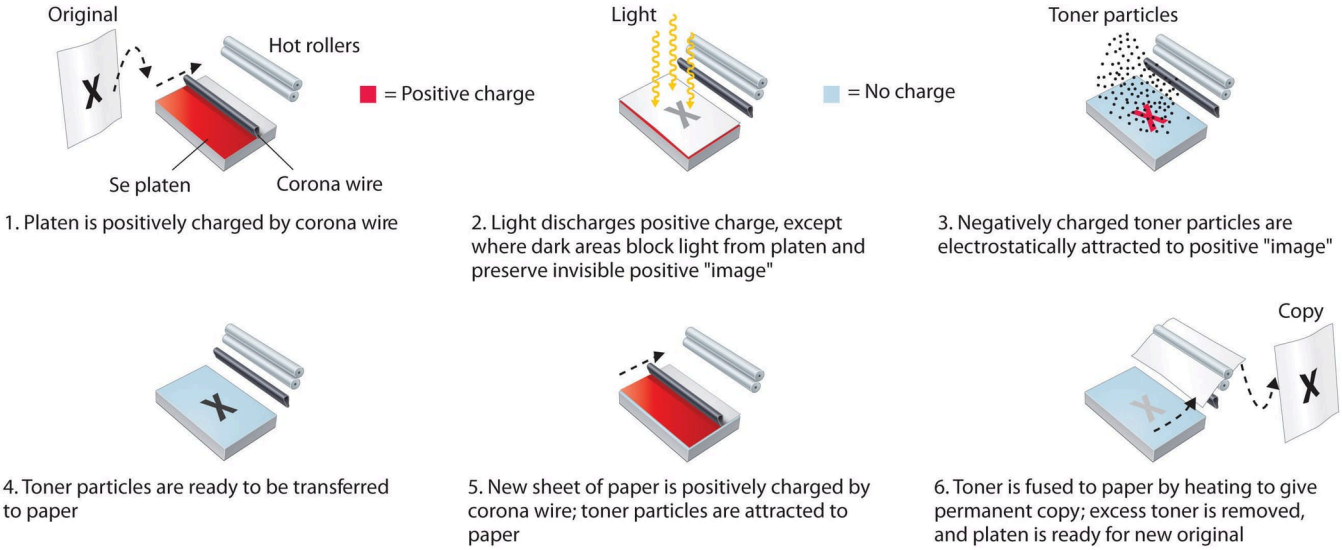


Figure 22.6.1: The Chemistry of Photocopying. Because amorphous selenium is a photosensitive semiconductor, exposing an electrostatically charged Se film to light causes the positive charge on the film to be discharged in all areas that are white in the original. Dark areas in the original block the light and generate an invisible, positively charged image. To produce an image on paper, negatively charged toner particles are attracted to the positive image, transferred to a negatively charged sheet of blank paper, and fused with the paper at high temperature to give a permanent image.

The heaviest chalcogen, polonium, was isolated after an extraordinary effort by Marie Curie. Although she was never able to obtain macroscopic quantities of the element, which she named for her native country of Poland, she demonstrated that its chemistry required it to be assigned to group 16. Marie Curie was awarded a second Nobel Prize in Chemistry in 1911 for the discovery of radium and polonium.

Preparation and General Properties of the Group 16 Elements

Oxygen is by far the most abundant element in Earth's crust and in the hydrosphere (about 44% and 86% by mass, respectively). The same process that is used to obtain nitrogen from the atmosphere produces pure oxygen. Oxygen can also be obtained by the electrolysis of water, the decomposition of alkali metal or alkaline earth peroxides or superoxides, or the thermal decomposition of simple inorganic salts, such as potassium chlorate in the presence of a catalytic amount of MnO_2:

$$2\mathrm{KClO_3(s)} \overset{\underset{\Delta}{\mathrm{MnO_2(s)}}}{\rightleftharpoons} 2\mathrm{KCl(s)} + 3\mathrm{O_2(g)} \tag{22.6.1}$$

Unlike oxygen, sulfur is not very abundant, but it is found as elemental sulfur in rock formations overlying salt domes, which often accompany petroleum deposits (Figure 22.6.1). Sulfur is also recovered from H_2S and organosulfur compounds in crude oil and coal and from metal sulfide ores such as pyrite (FeS_2).



Pyrite (FeS_2). Because of its lustrous golden yellow cubic crystals, FeS_2 is sometimes mistaken for gold, giving rise to its common name "fool's gold." Real gold, however, is much denser than FeS_2, and gold is soft and malleable rather than hard and brittle.

Because selenium and tellurium are chemically similar to sulfur, they are usually found as minor contaminants in metal sulfide ores and are typically recovered as by-products. Even so, they are as abundant in Earth's crust as silver, palladium, and gold. One of the best sources of selenium and tellurium is the "slime" deposited during the electrolytic purification of copper. Both of these elements are notorious for the vile odors of many of their compounds. For example, when the body absorbs even trace amounts of tellurium, dimethyltellurium [$(CH_3)_2Te$] is produced and slowly released in the breath and perspiration, resulting in an intense garlic-like smell that is commonly called "tellurium breath."

With their ns^2np^4 electron configurations, the chalcogens are two electrons short of a filled valence shell. Thus in reactions with metals, they tend to acquire two additional electrons to form compounds in the –2 oxidation state. This tendency is greatest for oxygen, the chalcogen with the highest electronegativity. The heavier, less electronegative chalcogens can lose either four np electrons or four np and two ns electrons to form compounds in the +4 and +6 oxidation state, respectively, as shown in Table Figure 22.6.1. As with the other groups, the lightest member in the group, in this case oxygen, differs greatly from the others in size, ionization energy, electronegativity, and electron affinity, so its chemistry is unique. Also as in the other groups, the second and third members (sulfur and selenium) have similar properties because of shielding effects. Only polonium is metallic, forming either the hydrated Po^{2+} or Po^{4+} ion in aqueous solution, depending on conditions.

Table 22.6.1: Selected Properties of the Group 16 Elements

Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
atomic mass (amu)	16.00	32.07	78.96	127.60	209
atomic number	8	16	34	52	84
atomic radius (pm)	48	88	103	123	135
atomic symbol	O	S	Se	Te	Po
density (g/cm^3) at 25°C	1.31 (g/L)	2.07	4.81	6.24	9.20
electron affinity (kJ/mol)	–141	–200	–195	–190	–180
electronegativity	3.4	2.6	2.6	2.1	2.0
first ionization energy (kJ/mol)	1314	1000	941	869	812
***The configuration shown does not include filled d and f subshells.**					
†The values cited for the hexacations are for six-coordinate ions and are only estimated values.					

Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
ionic radius (pm)†	140 (–2)	184 (–2), 29 (+6)	198 (–2), 42 (+6)	221 (–2), 56 (+6)	230 (–2), 97 (+4)
melting point/boiling point (°C)	–219/–183	115/445	221/685	450/988	254/962
normal oxidation state(s)	–2	+6, +4, –2	+6, +4, –2	+6, +4, –2	+2 (+4)
product of reaction with H_2	H_2O	H_2S	H_2Se	none	none
product of reaction with N_2	NO, NO_2	none	none	none	none
product of reaction with O_2	—	SO_2	SeO_2	TeO_2	PoO_2
product of reaction with X_2	O_2F_2	SF_6, S_2Cl_2, S_2Br_2	SeF_6, SeX_4	TeF_6, TeX_4	PoF_4, $PoCl_2$, $PoBr_2$
standard reduction potential (E°, V) (E^0 → H_2E in acidic solution)	+1.23	+0.14	–0.40	–0.79	–1.00
type of oxide	—	acidic	acidic	amphoteric	basic
valence electron configuration*	$2s^22p^4$	$3s^23p^4$	$4s^24p^4$	$5s^25p^4$	$6s^26p^4$
***The configuration shown does not include filled d and f subshells.**					
†The values cited for the hexacations are for six-coordinate ions and are only estimated values.					

Reactions and Compounds of Oxygen

As in groups 14 and 15, the lightest group 16 member has the greatest tendency to form multiple bonds. Thus elemental oxygen is found in nature as a diatomic gas that contains a net double bond: O=O. As with nitrogen, electrostatic repulsion between lone pairs of electrons on adjacent atoms prevents oxygen from forming stable catenated compounds. In fact, except for O_2, all compounds that contain O–O bonds are potentially explosive. Ozone, peroxides, and superoxides are all potentially dangerous in pure form. Ozone (O_3), one of the most powerful oxidants known, is used to purify drinking water because it does not produce the characteristic taste associated with chlorinated water. Hydrogen peroxide (H_2O_2) is so thermodynamically unstable that it has a tendency to undergo explosive decomposition when impure:

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)} \qquad \Delta G^o = -119\ kJ/mol \tag{22.6.2}$$

As in groups 14 and 15, the lightest element in group 16 has the greatest tendency to form multiple bonds.

Despite the strength of the O=O bond (D_{O_2} = 494 kJ/mol), O_2 is extremely reactive, reacting directly with nearly all other elements except the noble gases. Some properties of O_2 and related species, such as the peroxide and superoxide ions, are in Table 22.6.2 . With few exceptions, the chemistry of oxygen is restricted to negative oxidation states because of its high electronegativity (χ = 3.4). Unlike the other chalcogens, oxygen does not form compounds in the +4 or +6 oxidation state. Oxygen is second only to fluorine in its ability to stabilize high oxidation states of metals in both ionic and covalent compounds. For example, AgO is a stable solid that contains silver in the unusual Ag(II) state, whereas OsO_4 is a volatile solid that contains Os(VIII). Because oxygen is so electronegative, the O–H bond is highly polar, creating a large bond dipole moment that makes hydrogen bonding much more important for compounds of oxygen than for similar compounds of the other chalcogens.

Table 22.6.2: Some Properties of O_2 and Related Diatomic Species

Species	Bond Order	Number of Unpaired e^-	O–O Distance (pm)*
O_2^+	2.5	1	112
O_2	2	2	121
***Source of data: Lauri Vaska, "Dioxygen-Metal Complexes: Toward a Unified View," Accounts of Chemical Research 9 (1976): 175.**			

Species	Bond Order	Number of Unpaired e^-	O–O Distance (pm)*
O_2^-	1.5	1	133
O_2^{2-}	1	0	149
***Source of data: Lauri Vaska, "Dioxygen-Metal Complexes: Toward a Unified View," Accounts of Chemical Research 9 (1976): 175.**			

Metal oxides are usually basic, and nonmetal oxides are acidic, whereas oxides of elements that lie on or near the diagonal band of semimetals are generally amphoteric. A few oxides, such as CO and PbO_2, are neutral and do not react with water, aqueous acid, or aqueous base. Nonmetal oxides are typically covalent compounds in which the bonds between oxygen and the nonmetal are polarized ($E^{\delta+}$–$O^{\delta-}$). Consequently, a lone pair of electrons on a water molecule can attack the partially positively charged E atom to eventually form an oxoacid. An example is reacting sulfur trioxide with water to form sulfuric acid:

$$H_2O_{(l)} + SO_{3(g)} \rightarrow H_2SO_{4(aq)} \tag{22.6.3}$$

The oxides of the semimetals and of elements such as Al that lie near the metal/nonmetal dividing line are amphoteric, as we expect:

$$Al_2O_{3(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)} \tag{22.6.4}$$

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} \tag{22.6.5}$$

Oxides of metals tend to be basic, oxides of nonmetals tend to be acidic, and oxides of elements in or near the diagonal band of semimetals are generally amphoteric.

Example 22.6.1

For each reaction, explain why the given products form.

a. $Ga_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Ga(OH)_4^-(aq)$
b. $3H_2O_2(aq) + 2MnO_4^-(aq) + 2H^+(aq) \rightarrow 3O_2(g) + 2MnO_2(s) + 4H_2O(l)$
c. $KNO_3(s) \xrightarrow{\Delta} KNO(s) + O_2(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. Gallium is a metal. We expect the oxides of metallic elements to be basic and therefore not to react with aqueous base. A close look at the periodic table, however, shows that gallium is close to the diagonal line of semimetals. Moreover, aluminum, the element immediately above gallium in group 13, is amphoteric. Consequently, we predict that gallium will behave like aluminum (Equation 22.6.5).
b. Hydrogen peroxide is an oxidant that can accept two electrons per molecule to give two molecules of water. With a strong oxidant, however, H_2O_2 can also act as a reductant, losing two electrons (and two protons) to produce O_2. Because the other reactant is permanganate, which is a potent oxidant, the only possible reaction is a redox reaction in which permanganate is the oxidant and hydrogen peroxide is the reductant. Recall that reducing permanganate often gives MnO_2, an insoluble brown solid. Reducing MnO_4^- to MnO_2 is a three-electron reduction, whereas the oxidation of H_2O_2 to O_2 is a two-electron oxidation.

c. This is a thermal decomposition reaction. Because KNO_3 contains nitrogen in its highest oxidation state (+5) and oxygen in its lowest oxidation state (−2), a redox reaction is likely. Oxidation of the oxygen in nitrate to atomic oxygen is a two-electron process per oxygen atom. Nitrogen is likely to accept two electrons because oxoanions of nitrogen are known only in the +5 (NO_3^-) and +3 (NO_2^-) oxidation states.

Exercise 22.6.2

Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $SiO_2(s) + H^+(aq) \rightarrow$
b. $NO(g) + O_2(g) \rightarrow$
c. $SO_3(g) + H_2O(l) \rightarrow$
d. $H_2O_2(aq) + I^-(aq) \rightarrow$

Answer

a. $SiO_2(s) + H^+(aq) \rightarrow$ no reaction
b. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
c. $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
d. $H_2O_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2OH^-(aq)$

Reactions and Compounds of the Heavier Chalcogens

Because most of the heavier chalcogens (group 16) and pnicogens (group 15) are nonmetals, they often form similar compounds. For example, both third-period elements of these groups (phosphorus and sulfur) form catenated compounds and form multiple allotropes. Consistent with periodic trends, the tendency to catenate decreases as we go down the column.

Sulfur and selenium both form a fairly extensive series of catenated species. For example, elemental sulfur forms S_8 rings packed together in a complex "crankshaft" arrangement (Figure 22.6.2), and molten sulfur contains long chains of sulfur atoms connected by S–S bonds. Moreover, both sulfur and selenium form polysulfides (S_n^{2-}) and polyselenides (Se_n^{2-}), with n ≤ 6. The only stable allotrope of tellurium is a silvery white substance whose properties and structure are similar to those of one of the selenium allotropes. Polonium, in contrast, shows no tendency to form catenated compounds. The striking decrease in structural complexity from sulfur to polonium is consistent with the decrease in the strength of single bonds and the increase in metallic character as we go down the group.

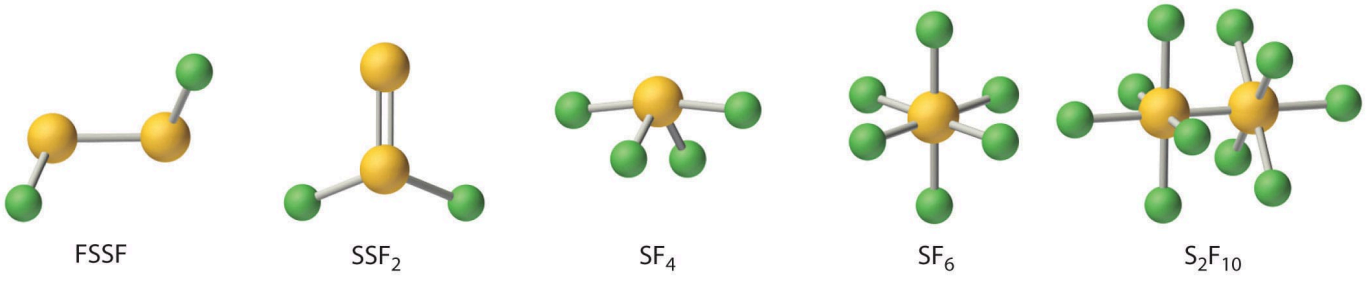


Figure 22.6.2: The Structures of the Known Fluorides of Sulfur. Five stable sulfur fluorides are known, containing sulfur in oxidation states ranging from +1 to +6. All are volatile molecular compounds that vary tremendously in stability and toxicity. Although both SF_6 and S_2F_{10} are very stable, S_2F_{10} is toxic and SF_6 is not. The other three are highly reactive substances.

As in group 15, the reactivity of elements in group 16 decreases from lightest to heaviest. For example, selenium and tellurium react with most elements but not as readily as sulfur does. As expected for nonmetals, sulfur, selenium, and tellurium do not react with water, aqueous acid, or aqueous base, but all dissolve in strongly oxidizing acids such as HNO_3 to form oxoacids such as H_2SO_4. In contrast to the other chalcogens, polonium behaves like a metal, dissolving in dilute HCl to form solutions that contain

the Po^{2+} ion.

> Just as with the other groups, the tendency to catenate, the strength of single bonds, and reactivity decrease down the group.

Fluorine reacts directly with all chalcogens except oxygen to produce the hexafluorides (YF_6), which are extraordinarily stable and unreactive compounds. Four additional stable fluorides of sulfur are known; thus sulfur oxidation states range from +1 to +6 (Figure 22.6.2). In contrast, only four fluorides of selenium (SeF_6, SeF_4, FSeSeF, and $SeSeF_2$) and only three of tellurium (TeF_4, TeF_6, and Te_2F_{10}) are known.

Direct reaction of the heavier chalcogens with oxygen at elevated temperatures gives the dioxides (YO_2), which exhibit a dramatic range of structures and properties. The dioxides become increasingly metallic in character down the group, as expected, and the coordination number of the chalcogen steadily increases. Thus SO_2 is a gas that contains V-shaped molecules (as predicted by the valence-shell electron-pair repulsion model), SeO_2 is a white solid with an infinite chain structure (each Se is three coordinate), TeO_2 is a light yellow solid with a network structure in which each Te atom is four coordinate, and PoO_2 is a yellow ionic solid in which each Po^{4+} ion is eight coordinate.

The dioxides of sulfur, selenium, and tellurium react with water to produce the weak, diprotic oxoacids (H_2YO_3—sulfurous, selenous, and tellurous acid, respectively). Both sulfuric acid and selenic acid (H_2SeO_4) are strong acids, but telluric acid [$Te(OH)_6$] is quite different. Because tellurium is larger than either sulfur or selenium, it forms weaker π bonds to oxygen. As a result, the most stable structure for telluric acid is $Te(OH)_6$, with six Te–OH bonds rather than Te=O bonds. Telluric acid therefore behaves like a weak triprotic acid in aqueous solution, successively losing the hydrogen atoms bound to three of the oxygen atoms. As expected for compounds that contain elements in their highest accessible oxidation state (+6 in this case), sulfuric, selenic, and telluric acids are oxidants. Because the stability of the highest oxidation state decreases with increasing atomic number, telluric acid is a stronger oxidant than sulfuric acid.

> The stability of the highest oxidation state of the chalcogens decreases down the column.

Sulfur and, to a lesser extent, selenium react with carbon to form an extensive series of compounds that are structurally similar to their oxygen analogues. For example, CS_2 and CSe_2 are both volatile liquids that contain C=S or C=Se bonds and have the same linear structure as CO_2. Because these double bonds are significantly weaker than the C=O bond, however, CS_2, CSe_2, and related compounds are less stable and more reactive than their oxygen analogues. The chalcogens also react directly with nearly all metals to form compounds with a wide range of stoichiometries and a variety of structures. Metal chalcogenides can contain either the simple chalcogenide ion (Y^{2-}), as in Na_2S and FeS, or polychalcogenide ions (Y_n^{2-}), as in FeS_2 and Na_2S_5.

> The dioxides of the group 16 elements become increasingly basic, and the coordination number of the chalcogen steadily increases down the group.

Ionic chalcogenides like Na_2S react with aqueous acid to produce binary hydrides such as hydrogen sulfide (H_2S). Because the strength of the Y–H bond decreases with increasing atomic radius, the stability of the binary hydrides decreases rapidly down the group. It is perhaps surprising that hydrogen sulfide, with its familiar rotten-egg smell, is much more toxic than hydrogen cyanide (HCN), the gas used to execute prisoners in the “gas chamber.” Hydrogen sulfide at relatively low concentrations deadens the olfactory receptors in the nose, which allows it to reach toxic levels without detection and makes it especially dangerous.

Example 22.6.2

For each reaction, explain why the given product forms or no reaction occurs.

a. $SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$
b. $SF_6(g) + H_2O(l) \rightarrow$ no reaction
c. $2Se(s) + Cl_2(g) \rightarrow Se_2Cl_2(l)$

Given: balanced chemical equations

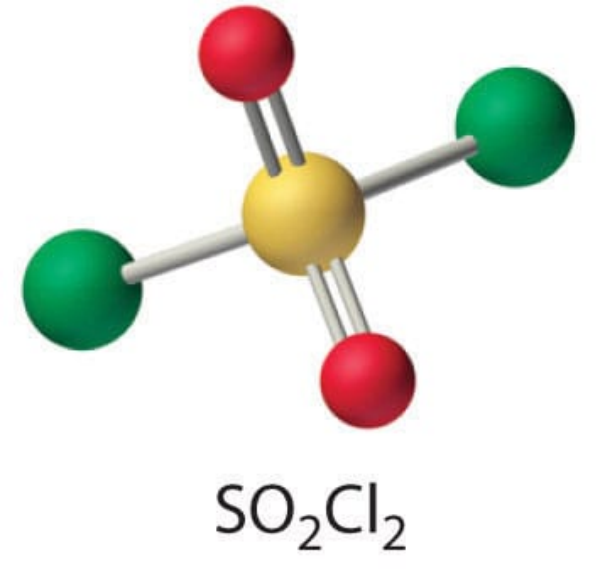
Asked for: why the given products (or no products) form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form or why no reaction occurs.

Solution

a. One of the reactants (Cl_2) is an oxidant. If the other reactant can be oxidized, then a redox reaction is likely. Sulfur dioxide contains sulfur in the +4 oxidation state, which is 2 less than its maximum oxidation state. Sulfur dioxide is also known to be a mild reducing agent in aqueous solution, producing sulfuric acid as the oxidation product. Hence a redox reaction is probable. The simplest reaction is the formation of SO_2Cl_2 (sulfuryl chloride), which is a tetrahedral species with two S–Cl and two S=O bonds.



b. Sulfur hexafluoride is a nonmetallic halide. Such compounds normally react vigorously with water to produce an oxoacid of the nonmetal and the corresponding hydrohalic acid. In this case, however, we have a highly stable species, presumably because all of sulfur's available orbitals are bonding orbitals. Thus SF_6 is not likely to react with water.

c. Here we have the reaction of a chalcogen with a halogen. The halogen is a good oxidant, so we can anticipate that a redox reaction will occur. Only fluorine is capable of oxidizing the chalcogens to a +6 oxidation state, so we must decide between $SeCl_4$ and Se_2Cl_2 as the product. The stoichiometry of the reaction determines which of the two is obtained: $SeCl_4$ or Se_2Cl_2.

Exercise 22.6.2

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $Te(s) + Na(s) \xrightarrow{\Delta}$
b. $SF_4(g) + H_2O(l) \rightarrow$
c. $CH_3SeSeCH_3(soln) + K(s) \rightarrow$
d. $Li_2Se(s) + H^+(aq) \rightarrow$

Answer

a. $Te(s) + 2Na(s) \rightarrow Na_2Te(s)$
b. $SF_4(g) + 3H_2O(l) \rightarrow H_2SO_3(aq) + 4HF(aq)$
c. $CH_3SeSeCH_3(soln) + 2K(s) \rightarrow 2KCH_3Se(soln)$

d. $Li_2Se(s) + 2H^+(aq) \rightarrow H_2Se(g) + 2Li^+(aq)$

Summary

The chalcogens have no stable metallic elements. The tendency to catenate, the strength of single bonds, and the reactivity all decrease moving down the group. Because the electronegativity of the chalcogens decreases down the group, so does their tendency to acquire two electrons to form compounds in the –2 oxidation state. The lightest member, oxygen, has the greatest tendency to form multiple bonds with other elements. It does not form stable catenated compounds, however, due to repulsions between lone pairs of electrons on adjacent atoms. Because of its high electronegativity, the chemistry of oxygen is generally restricted to compounds in which it has a negative oxidation state, and its bonds to other elements tend to be highly polar. Metal oxides are usually basic, and nonmetal oxides are acidic, whereas oxides of elements along the dividing line between metals and nonmetals are amphoteric. The reactivity, the strength of multiple bonds to oxygen, and the tendency to form catenated compounds all decrease down the group, whereas the maximum coordination numbers increase. Because Te=O bonds are comparatively weak, the most stable oxoacid of tellurium contains six Te–OH bonds. The stability of the highest oxidation state (+6) decreases down the group. Double bonds between S or Se and second-row atoms are weaker than the analogous C=O bonds because of reduced orbital overlap. The stability of the binary hydrides decreases down the group.

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22.7: Nitrogen

Like the group 14 elements, the lightest member of group 15, nitrogen, is found in nature as the free element, and the heaviest elements have been known for centuries because they are easily isolated from their ores. Although nitrogen is the most abundant element in the atmosphere, it was the last of the pnicogens (Group 15 elements) to be obtained in pure form. In 1772, Daniel Rutherford, working with Joseph Black (who discovered CO_2), noticed that a gas remained when CO_2 was removed from a combustion reaction. Antoine Lavoisier called the gas azote, meaning "no life," because it did not support life. When it was discovered that the same element was also present in nitric acid and nitrate salts such as KNO_3 (nitre), it was named nitrogen. About 90% of the nitrogen produced today is used to provide an inert atmosphere for processes or reactions that are oxygen sensitive, such as the production of steel, petroleum refining, and the packaging of foods and pharmaceuticals.

Preparation and General Properties of Nitrogen

Because the atmosphere contains several trillion tons of elemental nitrogen with a purity of about 80%, it is a huge source of nitrogen gas. Distillation of liquefied air yields nitrogen gas that is more than 99.99% pure, but small amounts of very pure nitrogen gas can be obtained from the thermal decomposition of sodium azide:

$$2\,\mathrm{NaN_3\,(s)} \xrightarrow{\Delta} 2\,\mathrm{Na\,(l)} + 3\,\mathrm{N_2\,(g)} \tag{22.7.1}$$

In contrast, Earth's crust is relatively poor in nitrogen. The only important nitrogen ores are large deposits of KNO_3 and $NaNO_3$ in the deserts of Chile and Russia, which were apparently formed when ancient alkaline lakes evaporated. Consequently, virtually all nitrogen compounds produced on an industrial scale use atmospheric nitrogen as the starting material. Phosphorus, which constitutes only about 0.1% of Earth's crust, is much more abundant in ores than nitrogen. Like aluminum and silicon, phosphorus is always found in combination with oxygen, and large inputs of energy are required to isolate it.

Reactions and Compounds of Nitrogen

Like carbon, nitrogen has four valence orbitals (one 2s and three 2p), so it can participate in at most four electron-pair bonds by using sp^3 hybrid orbitals. Unlike carbon, however, nitrogen does not form long chains because of repulsive interactions between lone pairs of electrons on adjacent atoms. These interactions become important at the shorter internuclear distances encountered with the smaller, second-period elements of groups 15, 16, and 17. Stable compounds with N–N bonds are limited to chains of no more than three N atoms, such as the azide ion (N_3^-).

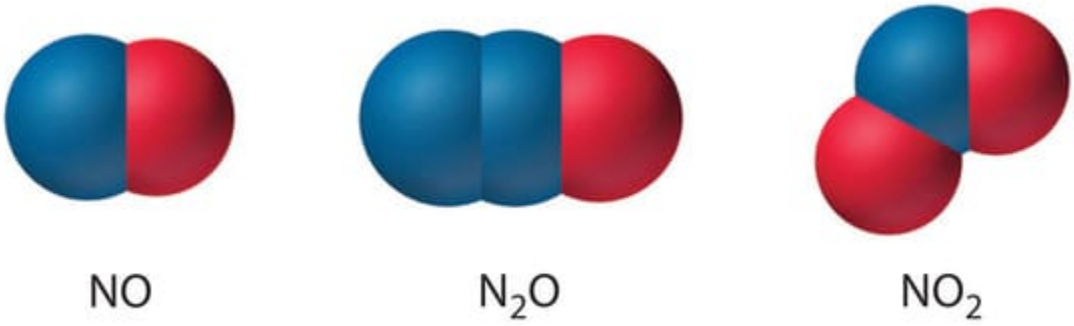
Nitrogen is the only pnicogen that normally forms multiple bonds with itself and other second-period elements, using π overlap of adjacent np orbitals. Thus the stable form of elemental nitrogen is N_2, whose N≡N bond is so strong ($D_{N\equiv N}$ = 942 kJ/mol) compared with the N–N and N=N bonds (D_{N-N} = 167 kJ/mol; $D_{N=N}$ = 418 kJ/mol) that all compounds containing N–N and N=N bonds are thermodynamically unstable with respect to the formation of N_2. In fact, the formation of the N≡N bond is so thermodynamically favored that virtually all compounds containing N–N bonds are potentially explosive.

Again in contrast to carbon, nitrogen undergoes only two important chemical reactions at room temperature: it reacts with metallic lithium to form lithium nitride, and it is reduced to ammonia by certain microorganisms. At higher temperatures, however, N_2 reacts with more electropositive elements, such as those in group 13, to give binary nitrides, which range from covalent to ionic in character. Like the corresponding compounds of carbon, binary compounds of nitrogen with oxygen, hydrogen, or other nonmetals are usually covalent molecular substances.

Few binary molecular compounds of nitrogen are formed by direct reaction of the elements. At elevated temperatures, N_2 reacts with H_2 to form ammonia, with O_2 to form a mixture of NO and NO_2, and with carbon to form cyanogen (N≡C–C≡N); elemental nitrogen does not react with the halogens or the other chalcogens. Nonetheless, all the binary nitrogen halides (NX_3) are known. Except for NF_3, all are toxic, thermodynamically unstable, and potentially explosive, and all are prepared by reacting the halogen with NH_3 rather than N_2. Both nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are thermodynamically unstable, with positive free energies of formation. Unlike NO, NO_2 reacts readily with excess water, forming a 1:1 mixture of nitrous acid (HNO_2) and nitric acid (HNO_3):

$$2\,NO_2\,(g) + H_2O\,(l) \longrightarrow HNO_2\,(aq) + HNO_3\,(aq) \tag{22.7.2}$$

Nitrogen also forms N_2O (dinitrogen monoxide, or nitrous oxide), a linear molecule that is isoelectronic with CO_2 and can be represented as $^{-}N{=}N^{+}{=}O$. Like the other two oxides of nitrogen, nitrous oxide is thermodynamically unstable. The structures of the three common oxides of nitrogen are as follows:



Few binary molecular compounds of nitrogen are formed by the direct reaction of the elements.

At elevated temperatures, nitrogen reacts with highly electropositive metals to form ionic nitrides, such as Li_3N and Ca_3N_2. These compounds consist of ionic lattices formed by M^{n+} and N^{3-} ions. Just as boron forms interstitial borides and carbon forms interstitial carbides, with less electropositive metals nitrogen forms a range of interstitial nitrides, in which nitrogen occupies holes in a close-packed metallic structure. Like the interstitial carbides and borides, these substances are typically very hard, high-melting materials that have metallic luster and conductivity.

Nitrogen also reacts with semimetals at very high temperatures to produce covalent nitrides, such as Si_3N_4 and BN, which are solids with extended covalent network structures similar to those of graphite or diamond. Consequently, they are usually high melting and chemically inert materials.

Ammonia (NH_3) is one of the few thermodynamically stable binary compounds of nitrogen with a nonmetal. It is not flammable in air, but it burns in an O_2 atmosphere:

$$4\,NH_3\,(g) + 3\,O_2\,(g) \longrightarrow 2\,N_2\,(g) + 6\,H_2O\,(g) \tag{22.7.3}$$

About 10% of the ammonia produced annually is used to make fibers and plastics that contain amide bonds, such as nylons and polyurethanes, while 5% is used in explosives, such as ammonium nitrate, TNT (trinitrotoluene), and nitroglycerine. Large amounts of anhydrous liquid ammonia are used as fertilizer.

Nitrogen forms two other important binary compounds with hydrogen. Hydrazoic acid (HN_3), also called hydrogen azide, is a colorless, highly toxic, and explosive substance. Hydrazine (N_2H_4) is also potentially explosive; it is used as a rocket propellant and to inhibit corrosion in boilers.

B, C, and N all react with transition metals to form interstitial compounds that are hard, high-melting materials.

Example 22.7.1

For each reaction, explain why the given products form when the reactants are heated.

a. $Sr\,(s) + N_2O\,(g) \xrightarrow{\Delta} SrO\,(s) + N_2\,(g)$
b. $NH_4NO_2\,(s) \xrightarrow{\Delta} N_2\,(g) + 2\,H_2O\,(g)$
c. $Pb(NO_3)_2\,(s) \xrightarrow{\Delta} PbO_2\,(s) + 2\,NO_2\,(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. As an alkali metal, strontium is a strong reductant. If the other reactant can act as an oxidant, then a redox reaction will occur. Nitrous oxide contains nitrogen in a low oxidation state (+1), so we would not normally consider it an oxidant. Nitrous oxide is, however, thermodynamically unstable ($\Delta H°_f > 0$ and $\Delta G°_f > 0$), and it can be reduced to N_2, which is a stable species. Consequently, we predict that a redox reaction will occur.
b. When a substance is heated, a decomposition reaction probably will occur, which often involves the release of stable gases. In this case, ammonium nitrite contains nitrogen in two different oxidation states (–3 and +3), so an internal redox reaction is a possibility. Due to its thermodynamic stability, N_2 is the probable nitrogen-containing product, whereas we predict that H and O will combine to form H_2O.
c. Again, this is probably a thermal decomposition reaction. If one element is in an usually high oxidation state and another in a low oxidation state, a redox reaction will probably occur. Lead nitrate contains the Pb^{2+} cation and the nitrate anion, which contains nitrogen in its highest possible oxidation state (+5). Hence nitrogen can be reduced, and we know that lead can be oxidized to the +4 oxidation state. Consequently, it is likely that lead(II) nitrate will decompose to lead(IV) oxide and nitrogen dioxide when heated. Even though PbO_2 is a powerful oxidant, the release of a gas such as NO_2 can often drive an otherwise unfavorable reaction to completion (Le Chatelier's principle). Note, however, that PbO_2 will probably decompose to PbO at high temperatures.

Exercise 22.7.1

Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $\mathrm{NO\,(g) + H_2O\,(l) \xrightarrow{\Delta}}$
b. $\mathrm{NH_4NO_3\,(s) \xrightarrow{\Delta}}$
c. $\mathrm{Sr\,(s) + N_2\,(g) \longrightarrow}$

Answer

a. $\mathrm{NO\,(g) + H_2O\,(l) \xrightarrow{\Delta}}$ no reaction
b. $\mathrm{NH_4NO_3\,(s) \xrightarrow{\Delta} N_2O\,(g) + 2\,H_2O\,(g)}$
c. $\mathrm{3\,Sr\,(s) + N_2\,(g) \longrightarrow Sr_3N_2\,(s)}$

Summary

Nitrogen behaves chemically like nonmetals, Nitrogen forms compounds in nine different oxidation states. Nitrogen does not form stable catenated compounds because of repulsions between lone pairs of electrons on adjacent atoms, but it does form multiple bonds with other second-period atoms. Nitrogen reacts with electropositive elements to produce solids that range from covalent to ionic in character. Reaction with electropositive metals produces ionic nitrides, reaction with less electropositive metals produces interstitial nitrides, and reaction with semimetals produces covalent nitrides.

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22.8: The Other Group 15 Elements - P, AS, Sb, and Bi

Learning Objectives

- To understand the trends in properties and reactivity of the group 14 elements: the pnicogens.

Antimony (Sb) was probably the first of the pnicogens to be obtained in elemental form and recognized as an element. Its atomic symbol comes from its Roman name: stibium. It is found in stibnite (Sb_2S_3), a black mineral that has been used as a cosmetic (an early form of mascara) since biblical times, and it is easily reduced to the metal in a charcoal fire (Figure 22.8.1). The Egyptians used antimony to coat copper objects as early as the third millennium BC, and antimony is still used in alloys to improve the tonal quality of bells.

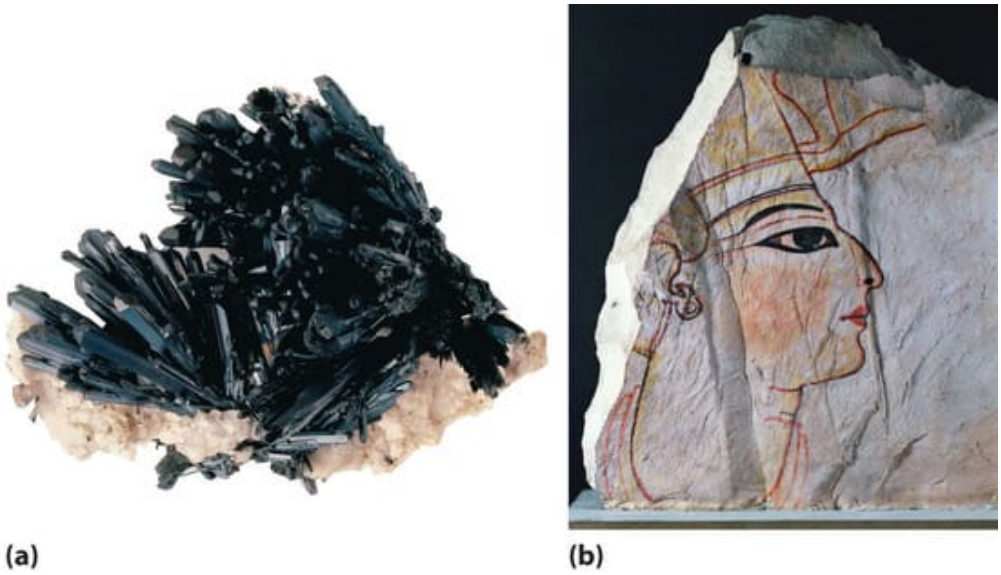


Figure 22.8.1: The Ancient Egyptians Used Finely Ground Antimony Sulfide for Eye Makeup. (a) Crystals of the soft black mineral stibnite (Sb_2S_3) on a white mineral matrix. (b) A fragment of an Egyptian painting on limestone from the 16th–13th centuries BC shows the use of ground stibnite ("kohl") as black eye shadow. Small vases of ground stibnite have been found among the funeral goods buried with Egyptian pharaohs.

In the form of its yellow sulfide ore, orpiment (As_2S_3), arsenic (As) has been known to physicians and professional assassins since ancient Greece, although elemental arsenic was not isolated until centuries later. The history of bismuth (Bi), in contrast, is more difficult to follow because early alchemists often confused it with other metals, such as lead, tin, antimony, and even silver (due to its slightly pinkish-white luster). Its name comes from the old German wismut, meaning "white metal." Bismuth was finally isolated in the 15th century, and it was used to make movable type for printing shortly after the invention of the Gutenberg printing process in 1440. Bismuth is used in printing because it is one of the few substances known whose solid state is less dense than the liquid. Consequently, its alloys expand as they cool, filling a mold completely and producing crisp, clear letters for typesetting.

Phosphorus was discovered in 1669 by the German alchemist Hennig Brandt, who was looking for the "philosophers' stone," a mythical substance capable of converting base metals to silver or gold. Believing that human urine was the source of the key ingredient, Brandt obtained several dozen buckets of urine, which he allowed to putrefy. The urine was distilled to dryness at high temperature and then condensed; the last fumes were collected under water, giving a waxy white solid that had unusual properties. For example, it glowed in the dark and burst into flames when removed from the water. (Unfortunately for Brandt, however, it did not turn lead into gold.) The element was given its current name (from the Greek phos, meaning "light," and phoros, meaning "bringing") in the 17th century. For more than a century, the only way to obtain phosphorus was the distillation of urine, but in 1769 it was discovered that phosphorus could be obtained more easily from bones. During the 19th century, the demand for phosphorus for matches was so great that battlefields and paupers' graveyards were systematically scavenged for bones. Early matches were pieces of wood coated with elemental phosphorus that were stored in an evacuated glass tube and ignited when

the tube was broken (which could cause unfortunate accidents if the matches were kept in a pocket!).

Unfortunately, elemental phosphorus is volatile and highly toxic. It is absorbed by the teeth and destroys bone in the jaw, leading to a painful and fatal condition called “phossy jaw,” which for many years was accepted as an occupational hazard of working in the match industry.

Preparation and General Properties of the Group 15 Elements

The three non-nitrogen pnicogens are much less abundant than nitrogen: arsenic is found in Earth’s crust at a concentration of about 2 ppm, antimony is an order of magnitude less abundant, and bismuth is almost as rare as gold. All three elements have a high affinity for the chalcogens and are usually found as the sulfide ores (M_2S_3), often in combination with sulfides of other heavy elements, such as copper, silver, and lead. Hence a major source of antimony and bismuth is flue dust obtained by smelting the sulfide ores of the more abundant metals.

In group 15, as elsewhere in the p block, we see large differences between the lightest element (N) and its congeners in size, ionization energy, electron affinity, and electronegativity (Table 22.8.1). The chemical behavior of the elements can be summarized rather simply: nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. With their ns^2np^3 valence electron configurations, all form compounds by losing either the three np valence electrons to form the +3 oxidation state or the three np and the two ns valence electrons to give the +5 oxidation state, whose stability decreases smoothly from phosphorus to bismuth. In addition, the relatively large magnitude of the electron affinity of the lighter pnicogens enables them to form compounds in the −3 oxidation state (such as NH_3 and PH_3), in which three electrons are formally added to the neutral atom to give a filled np subshell. Nitrogen has the unusual ability to form compounds in nine different oxidation states, including −3, +3, and +5. Because neutral covalent compounds of the trivalent pnicogens contain a lone pair of electrons on the central atom, they tend to behave as Lewis bases.

Table 22.8.1: Selected Properties of the Group 15 Elements

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
atomic symbol	N	P	As	Sb	Bi
atomic number	7	15	33	51	83
atomic mass (amu)	14.01	30.97	74.92	121.76	209.98
valence electron configuration*	$2s^22p^3$	$3s^23p^3$	$4s^24p^3$	$5s^25p^3$	$6s^26p^3$
melting point/boiling point (°C)	−210/−196	44.15/281[c]	817 (at 3.70 MPa)/603 (sublimes)[†]	631/1587	271/1564
density (g/cm^3) at 25°C	1.15 (g/L)	1.82[†]	5.75[‡]	6.68	9.79
atomic radius (pm)	56	98	114	133	143
first ionization energy (kJ/mol)	1402	1012	945	831	703
common oxidation state(s)	−3 to +5	+5, +3, −3	+5, +3	+5, +3	+3

***The configuration shown does not include filled d and f subshells.**

[†]For white phosphorus.

[‡]For gray arsenic.

[§]The values cited are for six-coordinate ions in the indicated oxidation states. The N^{5+}, P^{5+}, and As^{5+} ions are not known species.

[‖]The chemical form of the elements in these oxidation states varies considerably. For N, the reaction is $NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$; for P and As, it is $H_3EO_4 + 2H^+ + 2e^- \rightarrow H_3EO_3 + H_2O$; and for Sb it is $Sb_2O_5 + 4e^- + 10H^+ \rightarrow 2Sb^{3+} + 5H_2O$.

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
ionic radius (pm)[§]	146 (−3), 16 (+3)	212 (−3), 44 (+3)	58 (+3)	76 (+3), 60 (+5)	103 (+3)
electron affinity (kJ/mol)	0	−72	−78	−101	−91
electronegativity	3.0	2.2	2.2	2.1	1.9
standard reduction potential (E°, V) ($E^{V} \rightarrow E^{III}$ in acidic solution)[‖]	+0.93	−0.28	+0.56	+0.65	—
product of reaction with O_2	NO_2, NO	P_4O_6, P_4O_{10}	As_4O_6	Sb_2O_5	Bi_2O_3
type of oxide	acidic (NO_2), neutral (NO, N_2O)	acidic	acidic	amphoteric	basic
product of reaction with N_2	—	none	none	none	none
product of reaction with X_2	none	PX_3, PX_5	AsF_5, AsX_3	SbF_5, $SbCl_5$, $SbBr_3$, SbI_3	BiF_5, BiX_3
product of reaction with H_2	none	none	none	none	none
***The configuration shown does not include filled d and f subshells.**					
[†]For white phosphorus.					
[‡]For gray arsenic.					
[§]The values cited are for six-coordinate ions in the indicated oxidation states. The N^{5+}, P^{5+}, and As^{5+} ions are not known species.					
[‖]The chemical form of the elements in these oxidation states varies considerably. For N, the reaction is $NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$; for P and As, it is $H_3EO_4 + 2H^+ + 2e^- \rightarrow H_3EO_3 + H_2O$; and for Sb it is $Sb_2O_5 + 4e^- + 10H^+ \rightarrow 2Sb^{3+} + 5H_2O$.					

In group 15, the stability of the +5 oxidation state decreases from P to Bi.

Because neutral covalent compounds of the trivalent group 15 elements have a lone pair of electrons on the central atom, they tend to be Lewis bases.

Reactions and Compounds of the Heavier Pnicogens

Like the heavier elements of group 14, the heavier pnicogens form catenated compounds that contain only single bonds, whose stability decreases rapidly as we go down the group. For example, phosphorus exists as multiple allotropes, the most common of which is white phosphorus, which consists of P_4 tetrahedra and behaves like a typical nonmetal. As is typical of a molecular solid, white phosphorus is volatile, has a low melting point (44.1°C), and is soluble in nonpolar solvents. It is highly strained, with bond angles of only 60°, which partially explains why it is so reactive and so easily converted to more stable allotropes. Heating white phosphorus for several days converts it to red phosphorus, a polymer that is air stable, virtually insoluble, denser than white phosphorus, and higher melting, properties that make it much safer to handle. A third allotrope of phosphorus, black phosphorus, is prepared by heating the other allotropes under high pressure; it is even less reactive, denser, and higher melting than red phosphorus. As expected from their structures, white phosphorus is an electrical insulator, and red and black phosphorus are semiconductors. The three heaviest pnicogens—arsenic, antimony, and bismuth—all have a metallic luster, but they are brittle (not ductile) and relatively poor electrical conductors.

As in group 14, the heavier group 15 elements form catenated compounds that contain only single bonds, whose stability decreases as we go down the group.

The reactivity of the heavier pnicogens decreases as we go down the column. Phosphorus is by far the most reactive of the pnicogens, forming binary compounds with every element in the periodic table except antimony, bismuth, and the noble gases. Phosphorus reacts rapidly with O_2, whereas arsenic burns in pure O_2 if ignited, and antimony and bismuth react with O_2 only when heated. None of the pnicogens reacts with nonoxidizing acids such as aqueous HCl, but all dissolve in oxidizing acids such as HNO_3. Only bismuth behaves like a metal, dissolving in HNO_3 to give the hydrated Bi^{3+} cation.

The reactivity of the heavier group 15 elements decreases as we go down the column.

The heavier pnicogens can use energetically accessible 3d, 4d, or 5d orbitals to form dsp^3 or d^2sp^3 hybrid orbitals for bonding. Consequently, these elements often have coordination numbers of 5 or higher. Phosphorus and arsenic form halides (e.g., $AsCl_5$) that are generally covalent molecular species and behave like typical nonmetal halides, reacting with water to form the corresponding oxoacids (in this case, H_3AsO_4). All the pentahalides are potent Lewis acids that can expand their coordination to accommodate the lone pair of a Lewis base:

$$AsF_{5(soln)} + F^-_{(soln)} \rightarrow AsF^-_{6(soln)} \tag{22.8.1}$$

In contrast, bismuth halides have extended lattice structures and dissolve in water to produce hydrated ions, consistent with the stronger metallic character of bismuth.

Except for BiF_3, which is essentially an ionic compound, the trihalides are volatile covalent molecules with a lone pair of electrons on the central atom. Like the pentahalides, the trihalides react rapidly with water. In the cases of phosphorus and arsenic, the products are the corresponding acids, H_3PO_3 and H_3AsO_3, where E is P or As:

$$EX_{3(l)} + 3H_2O_{(l)} \rightarrow H_3EO_{3(aq)} + 3HX_{(aq)} \tag{22.8.2}$$

Phosphorus halides are also used to produce insecticides, flame retardants, and plasticizers.

Phosphorus has the greatest ability to form π bonds with elements such as O, N, and C.

With energetically accessible d orbitals, phosphorus and, to a lesser extent, arsenic are able to form π bonds with second-period atoms such as N and O. This effect is even more important for phosphorus than for silicon, resulting in very strong P–O bonds and even stronger P=O bonds. The first four elements in group 15 also react with oxygen to produce the corresponding oxide in the +3 oxidation state. Of these oxides, P_4O_6 and As_4O_6 have cage structures formed by inserting an oxygen atom into each edge of the P_4 or As_4 tetrahedron (part (a) in Figure 22.8.2), and they behave like typical nonmetal oxides. For example, P_4O_6 reacts with water to form phosphorous acid (H_3PO_3). Consistent with its position between the nonmetal and metallic oxides, Sb_4O_6 is amphoteric, dissolving in either acid or base. In contrast, Bi_2O_3 behaves like a basic metallic oxide, dissolving in acid to give solutions that contain the hydrated Bi^{3+} ion. The two least metallic elements of the heavier pnicogens, phosphorus and arsenic, form very stable oxides with the formula E_4O_{10} in the +5 oxidation state (part (b) in Figure 22.8.2. In contrast, Bi_2O_5 is so unstable that there is no absolute proof it exists.

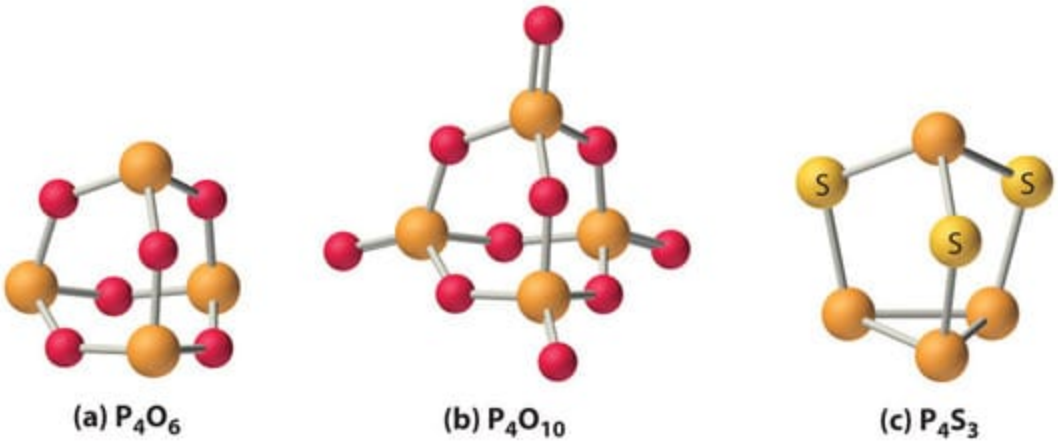


Figure 22.8.2: The Structures of Some Cage Compounds of Phosphorus. (a, b) The structures of P_4O_6 and P_4O_{10} are both derived from the structure of white phosphorus (P_4) by inserting an oxygen atom into each of the six edges of the P_4 tetrahedron; P_4O_{10} contains an additional terminal oxygen atom bonded to each phosphorus atom. (c) The structure of P_4S_3 is also derived from the structure of P_4 by inserting three sulfur atoms into three adjacent edges of the tetrahedron.

The heavier pnicogens form sulfides that range from molecular species with three-dimensional cage structures, such as P_4S_3 (part (c) in Figure 22.8.2), to layered or ribbon structures, such as Sb_2S_3 and Bi_2S_3, which are semiconductors. Reacting the heavier pnicogens with metals produces substances whose properties vary with the metal content. Metal-rich phosphides (such as M_4P) are hard, high-melting, electrically conductive solids with a metallic luster, whereas phosphorus-rich phosphides (such as MP_{15}) are lower melting and less thermally stable because they contain catenated P_n units. Many organic or organometallic compounds of the heavier pnicogens containing one to five alkyl or aryl groups are also known. Because of the decreasing strength of the pnicogen–carbon bond, their thermal stability decreases from phosphorus to bismuth.

> The thermal stability of organic or organometallic compounds of group 15 decreases down the group due to the decreasing strength of the pnicogen–carbon bond.

Example 22.8.1

For each reaction, explain why the given products form.

a. $\mathrm{Bi(s) + \frac{3}{2}Br(l) \rightarrow BiBr_3(s)}$
b. $2(CH_3)_3As(l) + O_2(g) \rightarrow 2(CH_3)_3As{=}O(s)$
c. $PBr_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HBr(aq)$
d. $As(s) + Ga(s) \xrightarrow{\Delta} GaAs(s)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution

a. Bromine is an oxidant, and bismuth is a metal that can be oxidized. Hence a redox reaction is likely to occur. To identify the product, recall that bismuth can form compounds in either the +3 or +5 oxidation state. The heaviest pnicogen, bismuth is rather difficult to oxidize to the +5 oxidation state because of the inert-pair effect. Hence the product will probably be bismuth(III) bromide.

b. Trimethylarsine, with a lone pair of electrons on the arsenic atom, can act as either a Lewis base or a reductant. If arsenic is oxidized by two electrons, then oxygen must be reduced, most probably by two electrons to the –2 oxidation state. Because As(V) forms strong bonds to oxygen due to π bonding, the expected product is $(CH_3)_3As{=}O$.
c. Phosphorus tribromide is a typical nonmetal halide. We expect it to react with water to produce an oxoacid of P(III) and the corresponding hydrohalic acid.Because of the strength of the P=O bond, phosphorous acid (H_3PO_3) is actually $HP(O)(OH)_2$, which contains a P=O bond and a P–H bond.
d. Gallium is a metal with a strong tendency to act as a reductant and form compounds in the +3 oxidation state. In contrast, arsenic is a semimetal. It can act as a reductant to form compounds in the +3 or +5 oxidation state, or it can act as an oxidant, accepting electrons to form compounds in the –3 oxidation state. If a reaction occurs, then a binary compound will probably form with a 1:1 ratio of the elements. GaAs is an example of a III-V compound, many of which are used in the electronics industry.

Exercise 22.8.1

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $PCl_5(s) + H_2O(l) \rightarrow$
b. $Bi_2O_5(s) \xrightarrow{\Delta}$
c. $Ca_3P_2(s) + H^+(aq) \rightarrow$
d. $NaNH_2(s) + PH_3(soln) \rightarrow$

Answer

a. $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$
b. $Bi_2O_5(s) \xrightarrow{\Delta} Bi_2O_3(s) + O_2(g)$
c. $Ca_3P_2(s) + 6H^+(aq) \rightarrow 2PH_3(g) + 3Ca^{2+}(aq)$
d. $NaNH_2(s) + PH_3(soln) \rightarrow NaPH_2(s) + NH_3(soln)$

Summary

The reactivity of the heavier group 15 elements decreases down the group, as does the stability of their catenated compounds. In group 15, nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. The stability of the +5 oxidation state decreases from phosphorus to bismuth because of the inert-pair effect. Due to their higher electronegativity, the lighter pnicogens form compounds in the –3 oxidation state. Because of the presence of a lone pair of electrons on the pnicogen, neutral covalent compounds of the trivalent pnicogens are Lewis bases. The reactivity of the pnicogens decreases with increasing atomic number. Compounds of the heavier pnicogens often have coordination numbers of 5 or higher and use dsp^3 or d^2sp^3 hybrid orbitals for bonding. Because phosphorus and arsenic have energetically accessible d orbitals, these elements form π bonds with second-period atoms such as O and N. Phosphorus reacts with metals to produce phosphides. Metal-rich phosphides are hard, high-melting, electrically conductive solids with metallic luster, whereas phosphorus-rich phosphides, which contain catenated phosphorus units, are lower melting and less thermally stable.

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22.9: Carbon

The elements of group 14 show a greater range of chemical behavior than any other family in the periodic table. Three of the five elements—carbon, tin, and lead—have been known since ancient times. For example, some of the oldest known writings are Egyptian hieroglyphics written on papyrus with ink made from lampblack, a finely divided carbon soot produced by the incomplete combustion of hydrocarbons (Figure 22.9.1). Activated carbon is an even more finely divided form of carbon that is produced from the thermal decomposition of organic materials, such as sawdust. Because it adsorbs many organic and sulfur-containing compounds, activated carbon is used to decolorize foods, such as sugar, and to purify gases and wastewater.



Figure 22.9.1: Very Small Particles of Noncrystalline Carbon Are Used to Make Black Ink. (a) Since ancient times, ink sticks have been the major source of black ink in Asia. Plant oils or resinous woods such as pine are burned, and the resulting soot (lampblack) is collected, mixed with binders such as animal glues and minerals, compressed into a solid stick, and allowed to dry. Liquid ink is made by rubbing the ink stick against the surface of a special stone ink dish with small amounts of water. (b) A 19th-century Japanese painting illustrates how ink is made from an ink stick.

Preparation and General Properties of Carbon

Elemental carbon, for example, ranks only 17th on the list of constituents of Earth's crust. Pure graphite is obtained by reacting coke, an amorphous form of carbon used as a reductant in the production of steel, with silica to give silicon carbide (SiC). This is then thermally decomposed at very high temperatures (2700°C) to give graphite:

$$\mathrm{SiO_2(s) + 3C(s) \xrightarrow{\Delta} SiC(s) + 2CO(g)} \tag{22.9.1}$$

$$\mathrm{SiC(s) \xrightarrow{\Delta} Si(s) + C(graphite)} \tag{22.9.2}$$

One allotrope of carbon, diamond, is metastable under normal conditions, with a $\Delta G°_f$ of 2.9 kJ/mol versus graphite. At pressures greater than 50,000 atm, however, the diamond structure is favored and is the most stable form of carbon. Because the structure of diamond is more compact than that of graphite, its density is significantly higher (3.51 g/cm^3 versus 2.2 g/cm^3). Because of its high thermal conductivity, diamond powder is used to transfer heat in electronic devices.

The most common sources of diamonds on Earth are ancient volcanic pipes that contain a rock called kimberlite, a lava that solidified rapidly from deep inside the Earth. Most kimberlite formations, however, are much newer than the diamonds they contain. In fact, the relative amounts of different carbon isotopes in diamond show that diamond is a chemical and geological "fossil" older than our solar system, which means that diamonds on Earth predate the existence of our sun. Thus diamonds were most likely created deep inside Earth from primordial grains of graphite present when Earth was formed (Figure 22.9.2). Gem-quality diamonds can now be produced synthetically and have chemical, optical, and physical characteristics identical to those of

the highest-grade natural diamonds.



Figure 22.9.2: Crystalline Samples of Carbon and Silicon, the Lightest Group 14 Elements. (a) The 78.86-carat Ahmadabad diamond, a historic Indian gem purchased in Gujarat in the 17th century by the French explorer Jean-Baptiste Tavernier and sold in 1995 for $4.3 million, is a rare example of a large single crystal of diamond, the less-stable allotrope of carbon.

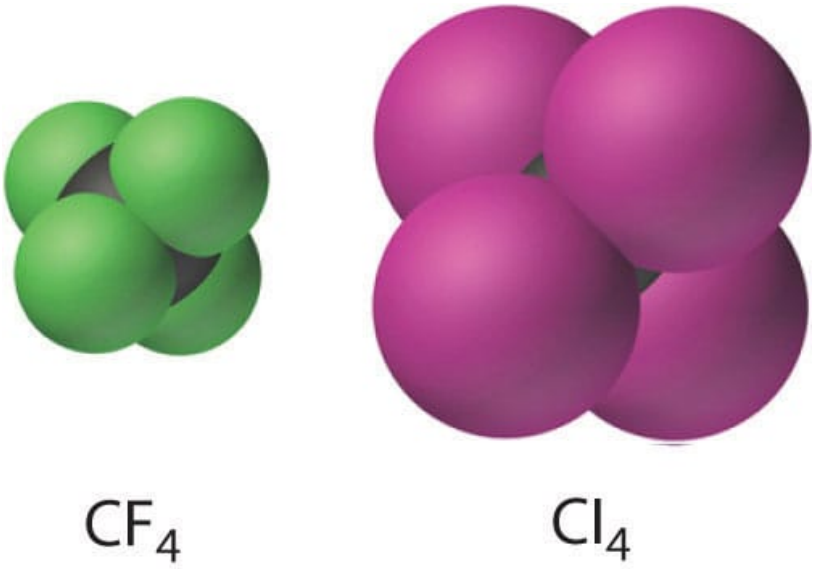
Reactions and Compounds of Carbon

Carbon is the building block of all organic compounds, including biomolecules, fuels, pharmaceuticals, and plastics, whereas inorganic compounds of carbon include metal carbonates, which are found in substances as diverse as fertilizers and antacid tablets, halides, oxides, carbides, and carboranes. Like boron in group 13, the chemistry of carbon differs sufficiently from that of its heavier congeners to merit a separate discussion.

The structures of the allotropes of carbon—diamond, graphite, fullerenes, and nanotubes—are distinct, but they all contain simple electron-pair bonds. Although it was originally believed that fullerenes were a new form of carbon that could be prepared only in the laboratory, fullerenes have been found in certain types of meteorites. Another possible allotrope of carbon has also been detected in impact fragments of a carbon-rich meteorite; it appears to consist of long chains of carbon atoms linked by alternating single and triple bonds, $(–C{\equiv}C–C{\equiv}C–)_n$. Carbon nanotubes (“buckytubes”) are being studied as potential building blocks for ultramicroscale detectors and molecular computers and as tethers for space stations. They are currently used in electronic devices, such as the electrically conducting tips of miniature electron guns for flat-panel displays in portable computers.

Although all the carbon tetrahalides (CX_4) are known, they are generally not obtained by the direct reaction of carbon with the elemental halogens (X_2) but by indirect methods such as the following reaction, where X is Cl or Br:

$$CH_{4(g)} + 4X_{2(g)} \rightarrow CX_{4(l,s)} + 4HX_{(g)} \tag{22.9.3}$$



The carbon tetrahalides all have the tetrahedral geometry predicted by the valence-shell electron-pair repulsion (VSEPR) model, as shown for CCl_4 and CI_4. Their stability decreases rapidly as the halogen increases in size because of poor orbital overlap and increased crowding. Because the C–F bond is about 25% stronger than a C–H bond, fluorocarbons are thermally and chemically more stable than the corresponding hydrocarbons, while having a similar hydrophobic character. A polymer of tetrafluoroethylene ($F_2C{=}CF_2$), analogous to polyethylene, is the nonstick Teflon lining found on many cooking pans, and similar compounds are used to make fabrics stain resistant (such as Scotch-Gard) or waterproof but breathable (such as Gore-Tex).

> The stability of the carbon tetrahalides decreases with increasing size of the halogen due to increasingly poor orbital overlap and crowding.

Carbon reacts with oxygen to form either CO or CO_2, depending on the stoichiometry. Carbon monoxide is a colorless, odorless, and poisonous gas that reacts with the iron in hemoglobin to form an Fe–CO unit, which prevents hemoglobin from binding, transporting, and releasing oxygen in the blood (see Figure 23.26). In the laboratory, carbon monoxide can be prepared on a small scale by dehydrating formic acid with concentrated sulfuric acid:

\[\mathrm{HCO_2H(l)}\xrightarrow{\mathrm{H_2SO_4(l)}}\mathrm{CO(g)}+\mathrm{H_3O^+(aq)}+\mathrm{HSO^-_4}\label{22.9.8} \]

Carbon monoxide also reacts with the halogens to form the oxohalides (COX_2). Probably the best known of these is phosgene ($Cl_2C{=}O$), which is highly poisonous and was used as a chemical weapon during World War I:

$$\mathrm{CO(g) + Cl_2(g) \xrightarrow{\Delta} Cl_2C{=}O(g)} \tag{22.9.4}$$

Despite its toxicity, phosgene is an important industrial chemical that is prepared on a large scale, primarily in the manufacture of polyurethanes.

Carbon dioxide can be prepared on a small scale by reacting almost any metal carbonate or bicarbonate salt with a strong acid. As is typical of a nonmetal oxide, CO_2 reacts with water to form acidic solutions containing carbonic acid (H_2CO_3). In contrast to its reactions with oxygen, reacting carbon with sulfur at high temperatures produces only carbon disulfide (CS_2):

$$\mathrm{C(s) + 2S(g) \xrightarrow{\Delta} CS_2(g)} \tag{22.9.5}$$

The selenium analog CSe_2 is also known. Both have the linear structure predicted by the VSEPR model, and both are vile smelling (and in the case of CSe_2, highly toxic), volatile liquids. The sulfur and selenium analogues of carbon monoxide, CS and CSe, are unstable because the C≡Y bonds (Y is S or Se) are much weaker than the C≡O bond due to poorer π orbital overlap.

> π bonds between carbon and the heavier chalcogenides are weak due to poor orbital overlap.

Binary compounds of carbon with less electronegative elements are called carbides. The chemical and physical properties of carbides depend strongly on the identity of the second element, resulting in three general classes: ionic carbides, interstitial carbides, and covalent carbides. The reaction of carbon at high temperatures with electropositive metals such as those of groups 1 and 2 and aluminum produces ionic carbides, which contain discrete metal cations and carbon anions. The identity of the anions depends on the size of the second element. For example, smaller elements such as beryllium and aluminum give methides such as Be_2C and Al_4C_3, which formally contain the C^{4-} ion derived from methane (CH_4) by losing all four H atoms as protons. In contrast, larger metals such as sodium and calcium give carbides with stoichiometries of Na_2C_2 and CaC_2. Because these carbides contain the C^{2-} ion, which is derived from acetylene (HC≡CH) by losing both H atoms as protons, they are more properly called acetylides. Reacting ionic carbides with dilute aqueous acid results in protonation of the anions to give the parent hydrocarbons: CH_4 or C_2H_2. For many years, miners' lamps used the reaction of calcium carbide with water to produce a steady supply of acetylene, which was ignited to provide a portable lantern.



19th-century miner's lamp. The lamp uses burning acetylene, produced by the slow reaction of calcium carbide with water, to provide light.

The reaction of carbon with most transition metals at high temperatures produces interstitial carbides. Due to the less electropositive nature of the transition metals, these carbides contain covalent metal–carbon interactions, which result in different properties: most interstitial carbides are good conductors of electricity, have high melting points, and are among the hardest substances known. Interstitial carbides exhibit a variety of nominal compositions, and they are often nonstoichiometric compounds whose carbon content can vary over a wide range. Among the most important are tungsten carbide (WC), which is used industrially in high-speed cutting tools, and cementite (Fe_3C), which is a major component of steel.

Elements with an electronegativity similar to that of carbon form covalent carbides, such as silicon carbide (SiC; Equation $22.9.1$) and boron carbide (B_4C). These substances are extremely hard, have high melting points, and are chemically inert. For example, silicon carbide is highly resistant to chemical attack at temperatures as high as 1600°C. Because it also maintains its strength at high temperatures, silicon carbide is used in heating elements for electric furnaces and in variable-temperature resistors.

> Carbides formed from group 1 and 2 elements are ionic. Transition metals form interstitial carbides with covalent metal–carbon interactions, and covalent carbides are chemically inert.

Example $22.9.1$

For each reaction, explain why the given product forms.

a. $CO(g) + Cl_2(g) \rightarrow Cl_2C{=}O(g)$
b. $CO(g) + BF_3(g) \rightarrow F_3B{:}C{\equiv}O(g)$
c. $Sr(s) + 2C(s) \xrightarrow{\Delta} SrC_2(s)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. Because the carbon in CO is in an intermediate oxidation state (+2), CO can be either a reductant or an oxidant; it is also a Lewis base. The other reactant (Cl_2) is an oxidant, so we expect a redox reaction to occur in which the carbon of CO is further oxidized. Because Cl_2 is a two-electron oxidant and the carbon atom of CO can be oxidized by two electrons to the +4 oxidation state, the product is phosgene ($Cl_2C{=}O$).
b. Unlike Cl_2, BF_3 is not a good oxidant, even though it contains boron in its highest oxidation state (+3). Nor can BF_3 behave like a reductant. Like any other species with only six valence electrons, however, it is certainly a Lewis acid. Hence an acid–base reaction is the most likely alternative, especially because we know that CO can use the lone pair of electrons on carbon to act as a Lewis base. The most probable reaction is therefore the formation of a Lewis acid–base adduct.
c. Typically, both reactants behave like reductants. Unless one of them can also behave like an oxidant, no reaction will occur. We know that Sr is an active metal because it lies far to the left in the periodic table and that it is more electropositive than carbon. Carbon is a nonmetal with a significantly higher electronegativity; it is therefore more likely to accept electrons in a redox reaction. We conclude, therefore, that Sr will be oxidized, and C will be reduced. Carbon forms ionic carbides with active metals, so the reaction will produce a species formally containing either C^{4-} or C_2^{2-}. Those that contain C^{4-} usually involve small, highly charged metal ions, so Sr^{2+} will produce the acetylide (SrC_2) instead.

Exercise 22.9.1

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $C(s) + \text{excess } O_2(g) \xrightarrow{\Delta}$
b. $C(s) + H_2O(l) \rightarrow$
c. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow$

Answer

a. $C(s) + \text{excess } O_2(g) \xrightarrow{\Delta} CO_2(g)$
b. $C(s) + H_2O(l) \rightarrow$ no reaction
c. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow CO_2(g) + NaHSO_4(aq) + H_2O(l)$

Summary

The stability of the carbon tetrahalides decreases as the halogen increases in size because of poor orbital overlap and steric crowding. Carbon forms three kinds of carbides with less electronegative elements: ionic carbides, which contain metal cations and C^{4-} (methide) or C_2^{2-} (acetylide) anions; interstitial carbides, which are characterized by covalent metal–carbon interactions and are among the hardest substances known; and covalent carbides, which have three-dimensional covalent network structures that make them extremely hard, high melting, and chemically inert.

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22.10: The Other Group 14 Elements- Si, Ge, Sn, and Pb

Learning Objectives

- To understand the trends in properties and reactivity of the group 14 elements.

Tin and lead oxides and sulfides are easily reduced to the metal by heating with charcoal, a discovery that must have occurred by accident when prehistoric humans used rocks containing their ores for a cooking fire. However, because tin and copper ores are often found together in nature, their alloy—bronze—was probably discovered before either element, a discovery that led to the Bronze Age. The heaviest element in group 14, lead, is such a soft and malleable metal that the ancient Romans used thin lead foils as writing tablets, as well as lead cookware and lead pipes for plumbing. (Recall that the atomic symbols for tin and lead come from their Latin names: Sn for stannum and Pb for plumbum.)

Although the first glasses were prepared from silica (silicon oxide, SiO_2) around 1500 BC, elemental silicon was not prepared until 1824 because of its high affinity for oxygen. Jöns Jakob Berzelius was finally able to obtain amorphous silicon by reducing Na_2SiF_6 with molten potassium. The crystalline element, which has a shiny blue-gray luster, was not isolated until 30 yr later. The last member of the group 14 elements to be discovered was germanium, which was found in 1886 in a newly discovered silver-colored ore by the German chemist Clemens Winkler, who named the element in honor of his native country.

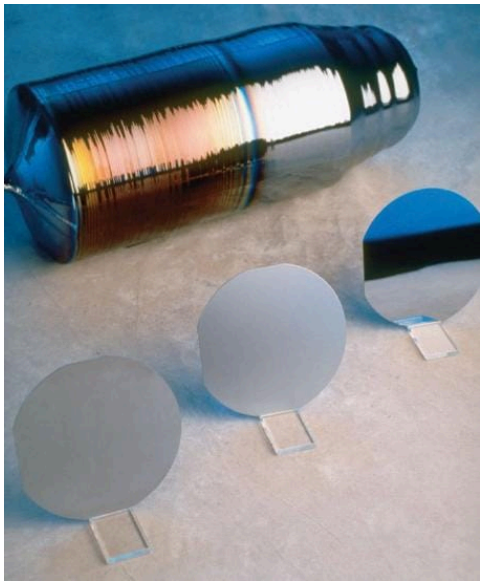


Figure 22.10.1: Large single crystals of highly purified silicon are the basis of the modern electronics industry. They are sliced into very thin wafers that are highly polished and then cut into smaller pieces for use as chips.

Preparation and General Properties of the Group 14 Elements

The natural abundance of the group 14 elements varies tremendously. Although oxygen is the most abundant element on Earth, the next most abundant is silicon, the next member of group 14. Pure silicon is obtained by reacting impure silicon with Cl_2 to give $SiCl_4$, followed by the fractional distillation of the impure $SiCl_4$ and reduction with H_2:

$$\mathrm{SiCl_4(l) + 2H_2(g) \xrightarrow{\Delta} Si(s) + 4HCl(g)} \tag{22.10.1}$$

Several million tons of silicon are annually produced with this method. Amorphous silicon containing residual amounts of hydrogen is used in photovoltaic devices that convert light to electricity, and silicon-based solar cells are used to power pocket calculators, boats, and highway signs, where access to electricity by conventional methods is difficult or expensive. Ultrapure silicon and germanium form the basis of the modern electronics industry (Figure 22.10.1).

In contrast to silicon, the concentrations of germanium and tin in Earth's crust are only 1–2 ppm. The concentration of lead, which is the end product of the nuclear decay of many radionuclides, is 13 ppm, making lead by far the most abundant of the heavy group 14 elements. No concentrated ores of germanium are known; like indium, germanium is generally recovered from flue dusts obtained by processing the ores of metals such as zinc. Because germanium is essentially transparent to infrared radiation, it is used in optical devices.

Tin and lead are soft metals that are too weak for structural applications, but because tin is flexible, corrosion resistant, and nontoxic, it is used as a coating in food packaging. A "tin can," for example, is actually a steel can whose interior is coated with a thin layer (1–2 μm) of metallic tin. Tin is also used in superconducting magnets and low-melting-point alloys such as solder and pewter. Pure lead is obtained by heating galena (PbS) in air and reducing the oxide (PbO) to the metal with carbon, followed by electrolytic deposition to increase the purity:

$$\mathrm{PbS(s)} + \frac{3}{2}\mathrm{O_2(g)} \xrightarrow{\Delta} \mathrm{PbO(s)} + \mathrm{SO_2(g)} \tag{22.10.2}$$

$$\mathrm{PbO(s)} + \mathrm{C(s)} \xrightarrow{\Delta} \mathrm{Pb(l)} + \mathrm{CO(g)} \tag{22.10.3}$$

or

$$\mathrm{PbO(s)} + \mathrm{CO(g)} \xrightarrow{\Delta} \mathrm{Pb(l)} + \mathrm{CO_2(g)} \tag{22.10.4}$$

By far the single largest use of lead is in lead storage batteries. The group 14 elements all have ns^2np^2 valence electron configurations. All form compounds in which they formally lose either the two np and the two ns valence electrons or just the two np valence electrons, giving a +4 or +2 oxidation state, respectively. Because covalent bonds decrease in strength with increasing atomic size and the ionization energies for the heavier elements of the group are higher than expected due to a higher Z_{eff}, the relative stability of the +2 oxidation state increases smoothly from carbon to lead.

> The relative stability of the +2 oxidation state increases, and the tendency to form catenated compounds decreases, from carbon to lead in group 14.

Recall that many carbon compounds contain multiple bonds formed by π overlap of singly occupied 2p orbitals on adjacent atoms. Compounds of silicon, germanium, tin, and lead with the same stoichiometry as those of carbon, however, tend to have different structures and properties. For example, CO_2 is a gas that contains discrete O=C=O molecules, whereas the most common form of SiO_2 is the high-melting solid known as quartz, the major component of sand. Instead of discrete SiO_2 molecules, quartz contains a three-dimensional network of silicon atoms that is similar to the structure of diamond but with an oxygen atom inserted between each pair of silicon atoms. Thus each silicon atom is linked to four other silicon atoms by bridging oxygen atoms.

The tendency to catenate—to form chains of like atoms—decreases rapidly as we go down group 14 because bond energies for both the E–E and E–H bonds decrease with increasing atomic number (where E is any group 14 element). Consequently, inserting a CH_2 group into a linear hydrocarbon such as n-hexane is exergonic ($\Delta G° = -45$ kJ/mol), whereas inserting an SiH_2 group into the silicon analogue of n-hexane (Si_6H_{14}) actually costs energy ($\Delta G° \approx +25$ kJ/mol). As a result of this trend, the thermal stability of catenated compounds decreases rapidly from carbon to lead.

In Table 22.10.1 we see, once again, that there is a large difference between the lightest element (C) and the others in size, ionization energy, and electronegativity. As in group 13, the second and third elements (Si and Ge) are similar, and there is a reversal in the trends for some properties, such as ionization energy, between the fourth and fifth elements (Sn and Pb). As for group 13, these effects can be explained by the presence of filled (n – 1)d and (n – 2)f subshells, whose electrons are relatively poor at screening the outermost electrons from the higher nuclear charge.

Table 22.10.1: Selected Properties of the Group 14 Elements

Property	Carbon	Silicon	Germanium	Tin	Lead
atomic symbol	C	Si	Ge	Sn	Pb
atomic number	6	14	32	50	82
atomic mass (amu)	12.01	28.09	72.64	118.71	207.2
valence electron configuration*	$2s^2 2p^2$	$3s^2 3p^2$	$4s^2 4p^2$	$5s^2 5p^2$	$6s^2 6p^2$
melting point/ boiling point (°C)	4489 (at 10.3 MPa)/3825	1414/3265	939/2833	232/2602	327/1749
density (g/cm^3) at 25°C	2.2 (graphite), 3.51 (diamond)	2.33	5.32	7.27(white)	11.30
atomic radius (pm)	77 (diamond)	111	125	145	154
first ionization energy (kJ/mol)	1087	787	762	709	716
most common oxidation state	+4	+4	+4	+4	+4
ionic radius (pm)†	≈29	≈40	53	69	77.5
electron affinity (kJ/mol)	−122	−134	−119	−107	−35
electronegativity	2.6	1.9	2.0	2.0	1.8
standard reduction potential (E°, V) (for $EO_2 \rightarrow E$ in acidic solution)	0.21	−0.86	−0.18	−0.12	0.79
product of reaction with O_2	CO_2, CO	SiO_2	GeO_2	SnO_2	PbO
type of oxide	acidic (CO_2)	acidic neutral (CO)	amphoteric	amphoteric	amphoteric
product of reaction with N_2	none	Si_3N_4	none	Sn_3N_4	none
product of reaction with X_2‡	CX_4	SiX_4	GeX_4	SnX_4	PbX_2
product of reaction with H_2	CH_4	none	none	none	none
***The configuration shown does not include filled d and f subshells.**					
†The values cited are for six-coordinate +4 ions in the most common oxidation state, except for C^{4+} and Si^{4+}, for which values for the four-coordinate ion are estimated.					
‡X is Cl, Br, or I. Reaction with F_2 gives the tetrafluorides (EF_4) for all group 14 elements, where E represents any group 14 element.					

The group 14 elements follow the same pattern as the group 13 elements in their periodic properties.

Reactions and Compounds of the Heavier Group 14 Elements

Although silicon, germanium, tin, and lead in their +4 oxidation states often form binary compounds with the same stoichiometry

as carbon, the structures and properties of these compounds are usually significantly different from those of the carbon analogues. Silicon and germanium are both semiconductors with structures analogous to diamond. Tin has two common allotropes: white (β) tin has a metallic lattice and metallic properties, whereas gray (α) tin has a diamond-like structure and is a semiconductor. The metallic β form is stable above 13.2°C, and the nonmetallic α form is stable below 13.2°C. Lead is the only group 14 element that is metallic in both structure and properties under all conditions.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 22.10.1*: Time lapse tin pest reaction.*

Based on its position in the periodic table, we expect silicon to be amphoteric. In fact, it dissolves in strong aqueous base to produce hydrogen gas and solutions of silicates, but the only aqueous acid that it reacts with is hydrofluoric acid, presumably due to the formation of the stable SiF_6^{2-} ion. Germanium is more metallic in its behavior than silicon. For example, it dissolves in hot oxidizing acids, such as HNO_3 and H_2SO_4, but in the absence of an oxidant, it does not dissolve in aqueous base. Although tin has an even more metallic character than germanium, lead is the only element in the group that behaves purely as a metal. Acids do not readily attack it because the solid acquires a thin protective outer layer of a Pb^{2+} salt, such as $PbSO_4$.

All group 14 dichlorides are known, and their stability increases dramatically as the atomic number of the central atom increases. Thus CCl_2 is dichlorocarbene, a highly reactive, short-lived intermediate that can be made in solution but cannot be isolated in pure form using standard techniques; $SiCl_2$ can be isolated at very low temperatures, but it decomposes rapidly above –150°C, and $GeCl_2$ is relatively stable at temperatures below 20°C. In contrast, $SnCl_2$ is a polymeric solid that is indefinitely stable at room temperature, whereas $PbCl_2$ is an insoluble crystalline solid with a structure similar to that of $SnCl_2$.

The stability of the group 14 dichlorides increases dramatically from carbon to lead.

Although the first four elements of group 14 form tetrahalides (MX_4) with all the halogens, only fluorine is able to oxidize lead to the +4 oxidation state, giving PbF_4. The tetrahalides of silicon and germanium react rapidly with water to give amphoteric oxides (where M is Si or Ge):

$$MX_{4(s,l)} + 2H_2O_{(l)} \rightarrow MO_{2(s)} + 4HX_{(aq)} \tag{22.10.5}$$

In contrast, the tetrahalides of tin and lead react with water to give hydrated metal ions. Because of the stability of its +2 oxidation state, lead reacts with oxygen or sulfur to form PbO or PbS, respectively, whereas heating the other group 14 elements with excess O_2 or S_8 gives the corresponding dioxides or disulfides, respectively. The dioxides of the group 14 elements become increasingly basic as we go down the group.

The dioxides of the group 14 elements become increasingly basic down the group.

Because the Si–O bond is even stronger than the C–O bond (~452 kJ/mol versus ~358 kJ/mol), silicon has a strong affinity for oxygen. The relative strengths of the C–O and Si–O bonds contradict the generalization that bond strengths decrease as the bonded atoms become larger. This is because we have thus far assumed that a formal single bond between two atoms can always be described in terms of a single pair of shared electrons. In the case of Si–O bonds, however, the presence of relatively low-energy, empty d orbitals on Si and nonbonding electron pairs in the p or sp^n hybrid orbitals of O results in a partial π bond (Figure 22.10.3). Due to its partial π double bond character, the Si–O bond is significantly stronger and shorter than would otherwise be expected. A similar interaction with oxygen is also an important feature of the chemistry of the elements that follow silicon in the third period (P, S, and Cl). Because the Si–O bond is unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.

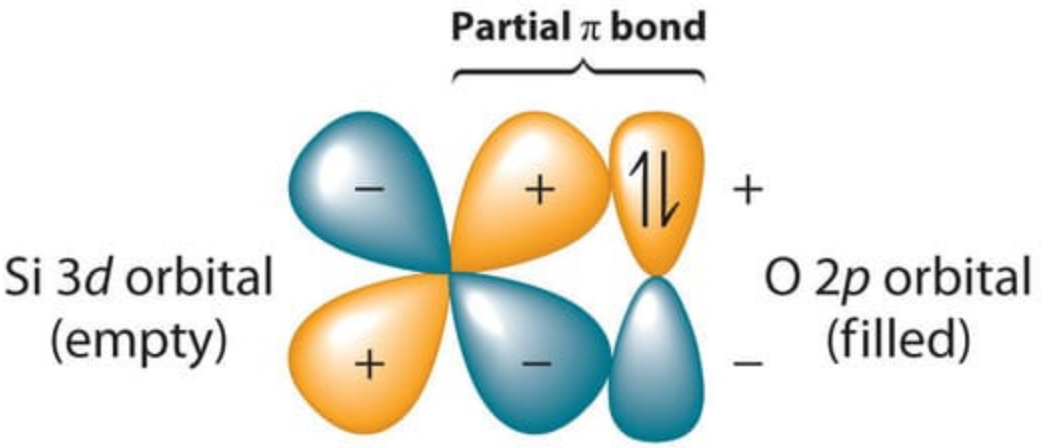
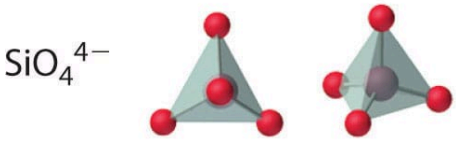


Figure 22.10.3: π Bonding between Silicon and Oxygen. Silicon has relatively low-energy, empty 3d orbitals that can interact with filled 2p hybrid orbitals on oxygen. This interaction results in a partial π bond in which both electrons are supplied by oxygen, giving the Si–O bond partial double bond character and making it significantly stronger (and shorter) than expected for a single bond.

Because silicon–oxygen bonds are unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.

Compounds with anions that contain only silicon and oxygen are called silicates, whose basic building block is the SiO_4^{4-} unit:



The number of oxygen atoms shared between silicon atoms and the way in which the units are linked vary considerably in different silicates. Converting one of the oxygen atoms from terminal to bridging generates chains of silicates, while converting two oxygen atoms from terminal to bridging generates double chains. In contrast, converting three or four oxygens to bridging generates a variety of complex layered and three-dimensional structures, respectively.

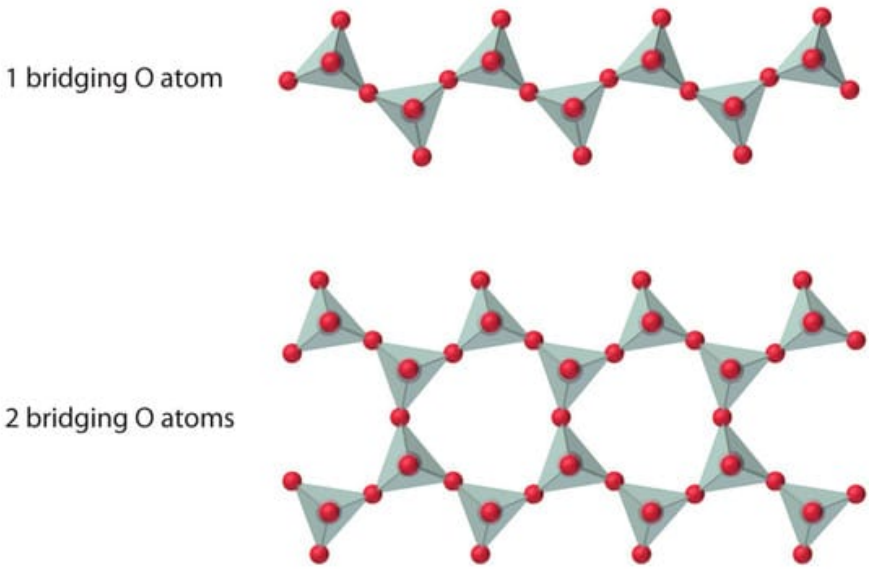


Figure 22.10.4). Because the cations in zeolites are readily exchanged, zeolites are used in laundry detergents as water-softening agents: the more loosely bound Na^+ ions inside the zeolite cavities are displaced by the more highly charged Mg^{2+} and Ca^{2+} ions present in hard water, which bind more tightly. Zeolites are also used as catalysts and for water purification.

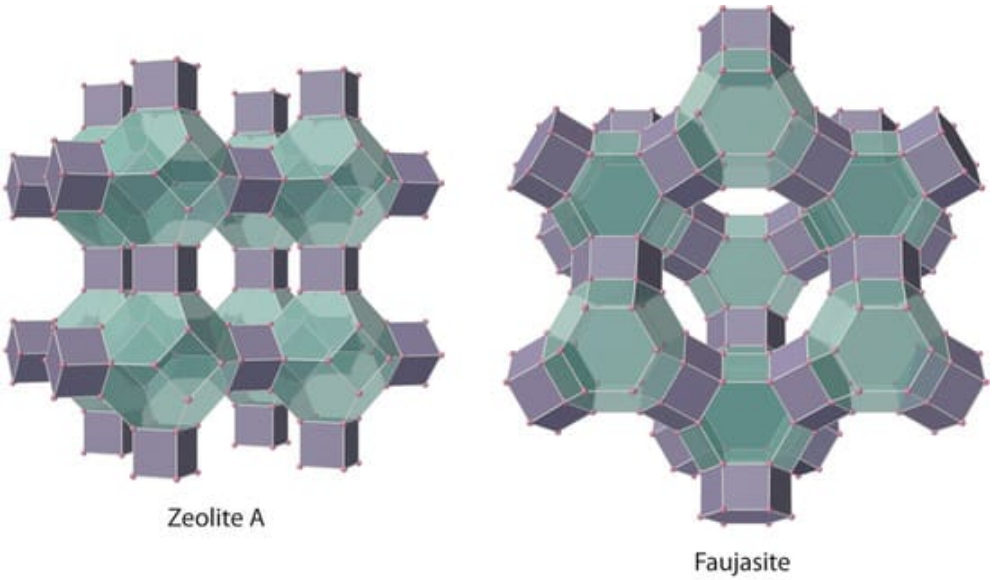


Figure 22.10.4: Zeolites Are Aluminosilicates with Large Cavities Connected by Channels. The cavities normally contain hydrated cations that are loosely bound to the oxygen atoms of the negatively charged framework by electrostatic interactions. The sizes and arrangements of the channels and cavities differ in different types of zeolites. For example, in zeolite A the aluminosilicate cages are arranged in a cubic fashion, and the channels connecting the cavities intersect at right angles. In contrast, the cavities in faujasite are much larger, and the channels intersect at 120° angles. In these idealized models, the oxygen atoms that connect each pair of silicon atoms have been omitted.

Silicon and germanium react with nitrogen at high temperature to form nitrides (M_3N_4):

$$3Si_{(l)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} \tag{22.10.6}$$

Silicon nitride has properties that make it suitable for high-temperature engineering applications: it is strong, very hard, and chemically inert, and it retains these properties to temperatures of about 1000°C.

Because of the diagonal relationship between boron and silicon, metal silicides and metal borides exhibit many similarities. Although metal silicides have structures that are as complex as those of the metal borides and carbides, few silicides are structurally similar to the corresponding borides due to the significantly larger size of Si (atomic radius 111 pm versus 87 pm for B). Silicides of active metals, such as Mg_2Si, are ionic compounds that contain the Si^{4-} ion. They react with aqueous acid to form silicon hydrides such as SiH_4:

$$Mg_2Si_{(s)} + 4H^+_{(aq)} \rightarrow 2Mg^{2+}_{(aq)} + SiH_{4(g)} \tag{22.10.7}$$

Unlike carbon, catenated silicon hydrides become thermodynamically less stable as the chain lengthens. Thus straight-chain and branched silanes (analogous to alkanes) are known up to only n = 10; the germanium analogues (germanes) are known up to n = 9. In contrast, the only known hydride of tin is SnH_4, and it slowly decomposes to elemental Sn and H_2 at room temperature. The simplest lead hydride (PbH_4) is so unstable that chemists are not even certain it exists. Because E=E and E≡E bonds become weaker with increasing atomic number (where E is any group 14 element), simple silicon, germanium, and tin analogues of alkenes, alkynes, and aromatic hydrocarbons are either unstable (Si=Si and Ge=Ge) or unknown. Silicon-based life-forms are therefore likely to be found only in science fiction.

The stability of group 14 hydrides decreases down the group, and E=E and E≡E bonds become weaker.

The only important organic derivatives of lead are compounds such as tetraethyllead [$(CH_3CH_2)_4Pb$]. Because the Pb–C bond is weak, these compounds decompose at relatively low temperatures to produce alkyl radicals (R·), which can be used to control the rate of combustion reactions. For 60 yr, hundreds of thousands of tons of lead were burned annually in automobile engines, producing a mist of lead oxide particles along the highways that constituted a potentially serious public health problem. The use of catalytic converters reduced the amount of carbon monoxide, nitrogen oxides, and hydrocarbons released into the atmosphere through automobile exhausts, but it did nothing to decrease lead emissions. Because lead poisons catalytic converters, however, its use as a gasoline additive has been banned in most of the world.

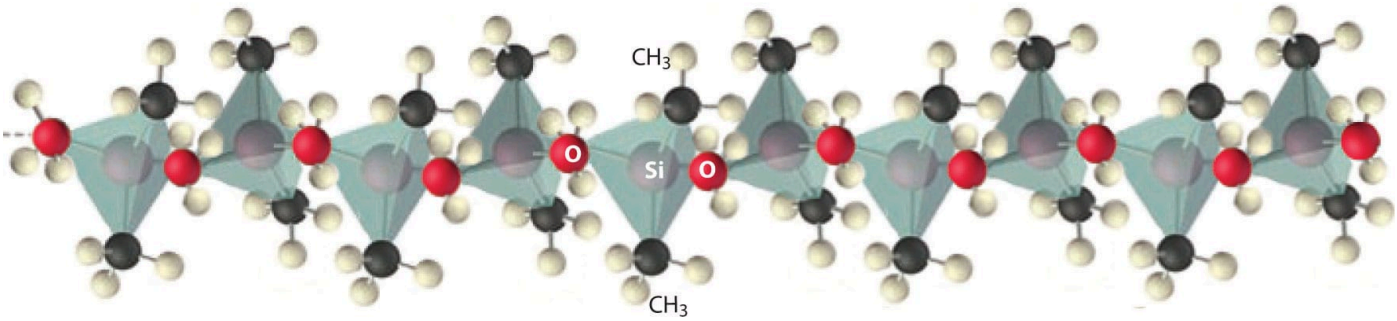


Figure 22.10.5 Silicones Are Polymers with Long Chains of Alternating Silicon and Oxygen Atoms. The structure of a linear silicone polymer is similar to that of quartz, but two of the oxygen atoms attached to each silicon atom are replaced by the carbon atoms of organic groups, such as the methyl groups (–CH_3) shown here. The terminal silicon atoms are bonded to three methyl groups. Silicones can be oily, waxy, flexible, or elastic, depending on the chain length, the extent of cross-linking between the chains, and the type of organic group.

Compounds that contain Si–C and Si–O bonds are stable and important. High-molecular-mass polymers called silicones contain an $(Si–O–)_n$ backbone with organic groups attached to Si (Figure 22.10.5). The properties of silicones are determined by the chain length, the type of organic group, and the extent of cross-linking between the chains. Without cross-linking, silicones are waxes or oils, but cross-linking can produce flexible materials used in sealants, gaskets, car polishes, lubricants, and even elastic materials, such as the plastic substance known as Silly Putty.



A child playing with Silly Putty, a silicone polymer with unusual mechanical properties. Gentle pressure causes Silly Putty to flow or stretch, but it cannot be flattened when hit with a hammer. This is called a "Non-Newtonian Fluid"

Example 22.10.2

For each reaction, explain why the given products form.

a. $Pb(s) + Cl_2(g) \rightarrow PbCl_2(s)$
b. $Mg_2Si(s) + 4H_2O(l) \rightarrow SiH_4(g) + 2Mg(OH)_2(s)$
c. $GeO_2(s) + 4OH^-(aq) \rightarrow GeO_4^{4-}(aq) + 2H_2O(l)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. Lead is a metal, and chlorine is a nonmetal that is a strong oxidant. Thus we can expect a redox reaction to occur in which the metal acts as a reductant. Although lead can form compounds in the +2 and +4 oxidation states, Pb^{4+} is a potent oxidant (the inert-pair effect). Because lead prefers the +2 oxidation state and chlorine is a weaker oxidant than fluorine, we expect $PbCl_2$ to be the product.

b. This is the reaction of water with a metal silicide, which formally contains the Si^{4-} ion. Water can act as either an acid or a base. Because the other compound is a base, we expect an acid–base reaction to occur in which water acts as an acid. Because Mg_2Si contains Si in its lowest possible oxidation state, however, an oxidation–reduction reaction is also a possibility. But water is a relatively weak oxidant, so an acid–base reaction is more likely. The acid (H_2O) transfers a proton to the base (Si^{4-}), which can accept four protons to form SiH_4. Proton transfer from water produces the OH^- ion, which will combine with Mg^{2+} to give magnesium hydroxide.

c. We expect germanium dioxide (GeO_2) to be amphoteric because of the position of germanium in the periodic table. It should dissolve in strong aqueous base to give an anionic species analogous to silicate.

Exercise 22.10.2

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $PbO_2(s) \xrightarrow{\Delta}$
b. $GeCl_4(s) + H_2O(l) \rightarrow$
c. $Sn(s) + HCl(aq) \rightarrow$

Answer

a. $\mathrm{PbO_2(s)} \xrightarrow{\Delta} \mathrm{PbO(s)} + \frac{1}{2}\mathrm{O_2(g)}$
b. $GeCl_4(s) + 2H_2O(l) \rightarrow GeO_2(s) + 4HCl(aq)$
c. $Sn(s) + 2HCl(aq) \rightarrow Sn^{2+}(aq) + H_2(g) + 2Cl^-(aq)$

Summary

The group 14 elements show the greatest diversity in chemical behavior of any group; covalent bond strengths decease with increasing atomic size, and ionization energies are greater than expected, increasing from C to Pb. Because the covalent bond strength decreases with increasing atomic size and greater-than-expected ionization energies due to an increase in Z_{eff}, the stability of the +2 oxidation state increases from carbon to lead. The tendency to form multiple bonds and to catenate decreases as the atomic number increases. Consistent with periodic trends, metallic behavior increases down the group. Silicon has a tremendous affinity for oxygen because of partial Si–O π bonding. Dioxides of the group 14 elements become increasingly basic down the group and their metallic character increases. Silicates contain anions that consist of only silicon and oxygen. Aluminosilicates are formed by replacing some of the Si atoms in silicates by Al atoms; aluminosilicates with three-dimensional framework structures are called zeolites. Nitrides formed by reacting silicon or germanium with nitrogen are strong, hard, and chemically inert. The hydrides become thermodynamically less stable down the group. Moreover, as atomic size increases, multiple bonds between or to the group 14 elements become weaker. Silicones, which contain an Si–O backbone and Si–C bonds, are high-molecular-mass polymers whose properties depend on their compositions.

Contributors and Attributions

- ◦ Anonymous

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22.11: Boron

Learning Objectives

- To understand the trends in properties and the reactivity of the group 13 elements.

Group 13 is the first group to span the dividing line between metals and nonmetals, so its chemistry is more diverse than that of groups 1 and 2, which include only metallic elements. Except for the lightest element (boron), the group 13 elements are all relatively electropositive; that is, they tend to lose electrons in chemical reactions rather than gain them. Although group 13 includes aluminum, the most abundant metal on Earth, none of these elements was known until the early 19th century because they are never found in nature in their free state. Elemental boron and aluminum, which were first prepared by reducing B_2O_3 and $AlCl_3$, respectively, with potassium, could not be prepared until potassium had been isolated and shown to be a potent reductant. Indium (In) and thallium (Tl) were discovered in the 1860s by using spectroscopic techniques, long before methods were available for isolating them. Indium, named for its indigo (deep blue-violet) emission line, was first observed in the spectrum of zinc ores, while thallium (from the Greek thallos, meaning "a young, green shoot of a plant") was named for its brilliant green emission line. Gallium (Ga; Mendeleev's eka-aluminum) was discovered in 1875 by the French chemist Paul Émile Lecoq de Boisbaudran during a systematic search for Mendeleev's "missing" element in group 13.

> Group 13 elements are never found in nature in their free state.

Preparation and General Properties of the Group 13 Elements

As reductants, the group 13 elements are less powerful than the alkali metals and alkaline earth metals. Nevertheless, their compounds with oxygen are thermodynamically stable, and large amounts of energy are needed to isolate even the two most accessible elements—boron and aluminum—from their oxide ores.

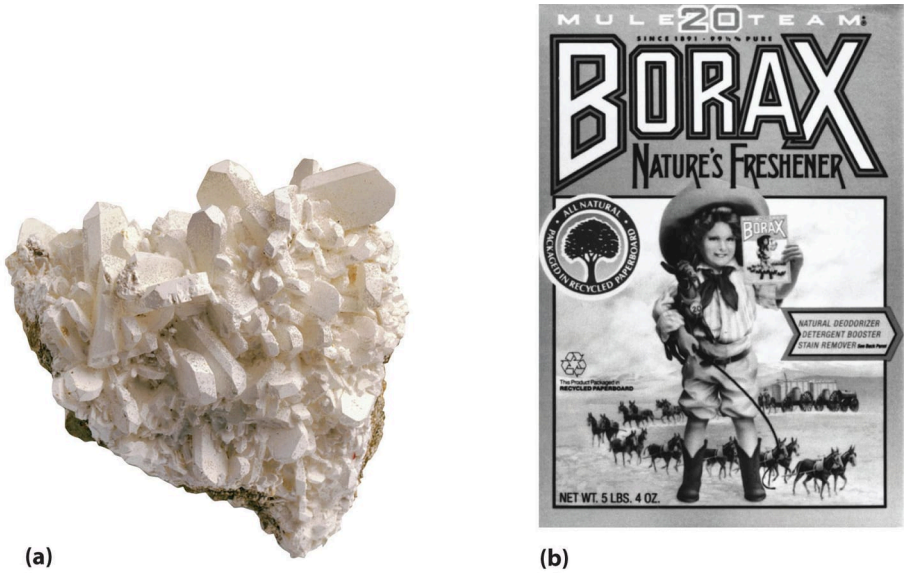


Figure 22.11.1: Borax Deposits. *(a) Concentrated deposits of crystalline borax [$Na_2B_4O_5(OH)_4{\cdot}8H_2O$] are found in ancient lake beds, such as the Mojave Desert and Death Valley in the western United States. (b) Borax is used in various cleaning products, including 20 Mule Team Borax, a laundry detergent named for the teams of 20 mules that hauled wagons full of borax from desert deposits to railroad terminals in the 1880s.*

Although boron is relatively rare (it is about 10,000 times less abundant than aluminum), concentrated deposits of borax [$Na_2B_4O_5(OH)_4{\cdot}8H_2O$] are found in ancient lake beds (Figure 22.11.1) and were used in ancient times for making glass and glazing pottery. Boron is produced on a large scale by reacting borax with acid to produce boric acid [$B(OH)_3$], which is then dehydrated to the oxide (B_2O_3). Reduction of the oxide with magnesium or sodium gives amorphous boron that is only about 95% pure:

$$\mathrm{Na_2B_4O_5(OH)_4 \cdot 8H_2O(s) \xrightarrow{acid} B(OH)_3(s) \xrightarrow{\Delta} B_2O_3(s)} \tag{22.11.1}$$

$$\mathrm{B_2O_3(s) + 3Mg(s) \xrightarrow{\Delta} 2B(s) + 3MgO(s)} \tag{22.11.2}$$

Pure, crystalline boron, however, is extremely difficult to obtain because of its high melting point (2300°C) and the highly corrosive nature of liquid boron. It is usually prepared by reducing pure BCl_3 with hydrogen gas at high temperatures or by the thermal decomposition of boron hydrides such as diborane (B_2H_6):

$$\mathrm{BCl_3(g) + \frac{3}{2}H_2(g) \rightarrow B(s) + 3HCl(g)} \tag{22.11.3}$$

$$B_2H_{6(g)} \rightarrow 2B_{(s)} + 3H_{2(g)} \tag{22.11.4}$$

The reaction shown in Equation 22.11.3 is used to prepare boron fibers, which are stiff and light. Hence they are used as structural reinforcing materials in objects as diverse as the US space shuttle and the frames of lightweight bicycles that are used in races such as the Tour de France. Boron is also an important component of many ceramics and heat-resistant borosilicate glasses, such as Pyrex, which is used for ovenware and laboratory glassware.

In contrast to boron, deposits of aluminum ores such as bauxite, a hydrated form of Al_2O_3, are abundant. With an electrical conductivity about twice that of copper on a weight for weight basis, aluminum is used in more than 90% of the overhead electric power lines in the United States. However, because aluminum–oxygen compounds are stable, obtaining aluminum metal from bauxite is an expensive process. Aluminum is extracted from oxide ores by treatment with a strong base, which produces the soluble hydroxide complex $[Al(OH)_4]^-$. Neutralization of the resulting solution with gaseous CO_2 results in the precipitation of $Al(OH)_3$:

$$2[Al(OH)_4]^-_{(aq)} + CO_{2(g)} \rightarrow 2Al(OH)_{3(s)} + CO^{2-}_{3(aq)} + H_2O_{(l)} \tag{22.11.5}$$

Thermal dehydration of $Al(OH)_3$ produces Al_2O_3, and metallic aluminum is obtained by the electrolytic reduction of Al_2O_3 using the **Hall–Heroult process**. Of the group 13 elements, only aluminum is used on a large scale: for example, each Boeing 777 airplane is about 50% aluminum by mass.

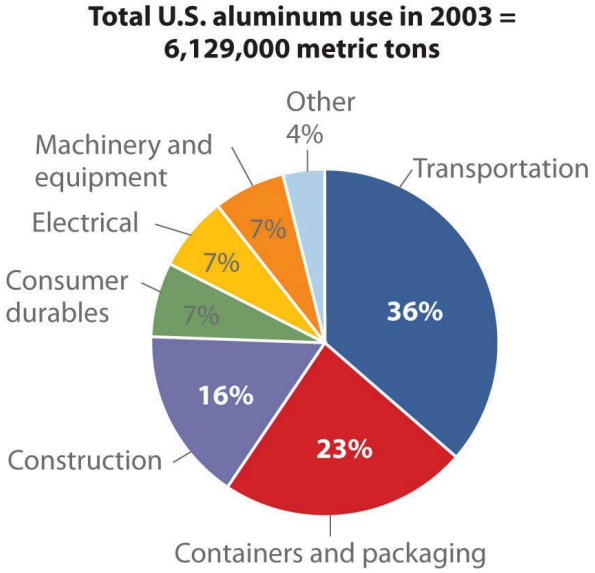


Figure 22.11.2: Source: Thomas D. Kelly and Grecia R. Matos, "Historical Statistics for Mineral and Material Commodities in the United States," US Geological Survey Data Series 140, 2010, accessed July 20, 2011, pubs.usgs.gov/ds/2005/140/.

The other members of group 13 are rather rare: gallium is approximately 5000 times less abundant than aluminum, and indium and thallium are even scarcer. Consequently, these metals are usually obtained as by-products in the processing of other metals. The extremely low melting point of gallium (29.6°C), however, makes it easy to separate from aluminum. Due to its low melting point and high boiling point, gallium is used as a liquid in thermometers that have a temperature range of almost 2200°C. Indium and thallium, the heavier group 13 elements, are found as trace impurities in sulfide ores of zinc and lead. Indium is used as a crushable seal for high-vacuum cryogenic devices, and its alloys are used as low-melting solders in electronic circuit boards.

Thallium, on the other hand, is so toxic that the metal and its compounds have few uses. Both indium and thallium oxides are released in flue dust when sulfide ores are converted to metal oxides and SO_2. Until relatively recently, these and other toxic elements were allowed to disperse in the air, creating large “dead zones” downwind of a smelter. The flue dusts are now trapped and serve as a relatively rich source of elements such as In and Tl (as well as Ge, Cd, Te, and As).

Table 22.11.1 summarizes some important properties of the group 13 elements. Notice the large differences between boron and aluminum in size, ionization energy, electronegativity, and standard reduction potential, which is consistent with the observation that boron behaves chemically like a nonmetal and aluminum like a metal. All group 13 elements have ns^2np^1 valence electron configurations, and all tend to lose their three valence electrons to form compounds in the +3 oxidation state. The heavier elements in the group can also form compounds in the +1 oxidation state formed by the formal loss of the single np valence electron. Because the group 13 elements generally contain only six valence electrons in their neutral compounds, these compounds are all moderately strong Lewis acids.

Table 22.11.1: Selected Properties of the Group 13 Elements

Property	Boron	Aluminum*	Gallium	Indium	Thallium
atomic symbol	B	Al	Ga	In	Tl
atomic number	5	13	31	49	81
atomic mass (amu)	10.81	26.98	69.72	114.82	204.38
valence electron configuration†	$2s^22p^1$	$3s^23p^1$	$4s^24p^1$	$5s^25p^1$	$6s^26p^1$
melting point/boiling point (°C)	2075/4000	660/2519	29.7/2204	156.6/2072	304/1473
density (g/cm^3) at 25°C	2.34	2.70	5.91	7.31	11.8
atomic radius (pm)	87	118	136	156	156
first ionization energy (kJ/mol)	801	578	579	558	589
most common oxidation state	+3	+3	+3	+3	+1
ionic radius (pm)‡	–25	54	62	80	162
electron affinity (kJ/mol)	–27	–42	–40	–39	–37
electronegativity	2.0	1.6	1.8	1.8	1.8
standard reduction potential (E°, V)	–0.87	–1.66	–0.55	–0.34	+0.741 of $M^{3+}(aq)$
product of reaction with O_2	B_2O_3	Al_2O_3	Ga_2O_3	In_2O_3	Tl_2O
type of oxide	acidic	amphoteric	amphoteric	amphoteric	basic

***This is the name used in the United States; the rest of the world inserts an extra i and calls it aluminium.**

†The configuration shown does not include filled d and f subshells.

‡The values cited are for six-coordinate ions in the most common oxidation state, except for Al^{3+}, for which the value for the four-coordinate ion is given. The B^{3+} ion is not a known species; the radius cited is an estimated four-coordinate value.

§X is Cl, Br, or I. Reaction with F_2 gives the trifluorides (MF_3) for all group 13 elements.

Property	Boron	Aluminum*	Gallium	Indium	Thallium
product of reaction with N_2	BN	AlN	GaN	InN	none
product of reaction with X_2[§]	BX_3	Al_2X_6	Ga_2X_6	In_2X_6	TlX
***This is the name used in the United States; the rest of the world inserts an extra i and calls it aluminium.**					
[†]The configuration shown does not include filled d and f subshells.					
[‡]The values cited are for six-coordinate ions in the most common oxidation state, except for Al^{3+}, for which the value for the four-coordinate ion is given. The B^{3+} ion is not a known species; the radius cited is an estimated four-coordinate value.					
[§]X is Cl, Br, or I. Reaction with F_2 gives the trifluorides (MF_3) for all group 13 elements.					

Neutral compounds of the group 13 elements are electron deficient, so they are generally moderately strong Lewis acids.

In contrast to groups 1 and 2, the group 13 elements show no consistent trends in ionization energies, electron affinities, and reduction potentials, whereas electronegativities actually increase from aluminum to thallium. Some of these anomalies, especially for the series Ga, In, Tl, can be explained by the increase in the effective nuclear charge (Z_{eff}) that results from poor shielding of the nuclear charge by the filled $(n - 1)d^{10}$ and $(n - 2)f^{14}$ subshells. Consequently, although the actual nuclear charge increases by 32 as we go from indium to thallium, screening by the filled 5d and 4f subshells is so poor that Z_{eff} increases significantly from indium to thallium. Thus the first ionization energy of thallium is actually greater than that of indium.

Anomalies in periodic trends among Ga, In, and Tl can be explained by the increase in the effective nuclear charge due to poor shielding.

Reactions and Compounds of Boron

Elemental boron is a semimetal that is remarkably unreactive; in contrast, the other group 13 elements all exhibit metallic properties and reactivity. We therefore consider the reactions and compounds of boron separately from those of other elements in the group. All group 13 elements have fewer valence electrons than valence orbitals, which generally results in delocalized, metallic bonding. With its high ionization energy, low electron affinity, low electronegativity, and small size, however, boron does not form a metallic lattice with delocalized valence electrons. Instead, boron forms unique and intricate structures that contain multicenter bonds, in which a pair of electrons holds together three or more atoms.

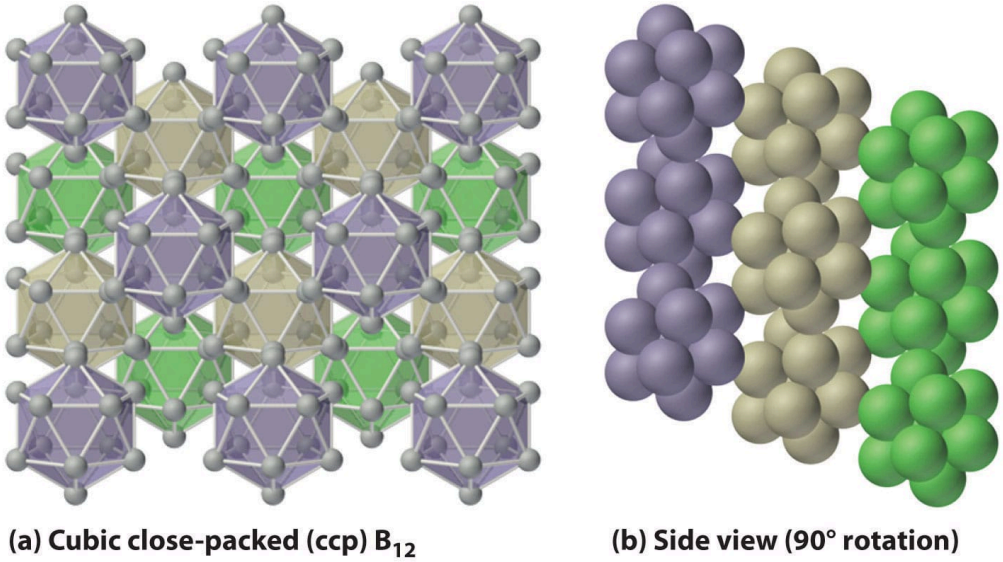


Figure 22.11.3: Solid Boron Contains B_{12} Icosahedra. Unlike metallic solids, elemental boron consists of a regular array of B_{12} icosahedra rather than individual boron atoms. Note that each boron atom in the B_{12} icosahedron is connected to five other boron atoms within the B_{12} unit. (a) The allotrope of boron with the simplest structure is α-rhombohedral boron, which consists of B_{12} octahedra in an almost cubic close-packed lattice. (b) A side view of the structure shows that icosahedra do not pack as efficiently as spheres, making the density of solid boron less than expected.

Elemental boron forms multicenter bonds, whereas the other group 13 elements exhibit metallic bonding.

The basic building block of elemental boron is not the individual boron atom, as would be the case in a metal, but rather the B_{12} icosahedron. Because these icosahedra do not pack together very well, the structure of solid boron contains voids, resulting in its low density (Figure 22.11.3). Elemental boron can be induced to react with many nonmetallic elements to give binary compounds that have a variety of applications. For example, plates of boron carbide (B_4C) can stop a 30-caliber, armor-piercing bullet, yet they weigh 10%–30% less than conventional armor. Other important compounds of boron with nonmetals include boron nitride (BN), which is produced by heating boron with excess nitrogen (Equation 22.11.6); boron oxide (B_2O_3), which is formed when boron is heated with excess oxygen (Equation 22.11.7); and the boron trihalides (BX_3), which are formed by heating boron with excess halogen (Equation 22.11.8).

$$2B(s) + N_2(g) \xrightarrow{\Delta} 2BN(s) \tag{22.11.6}$$

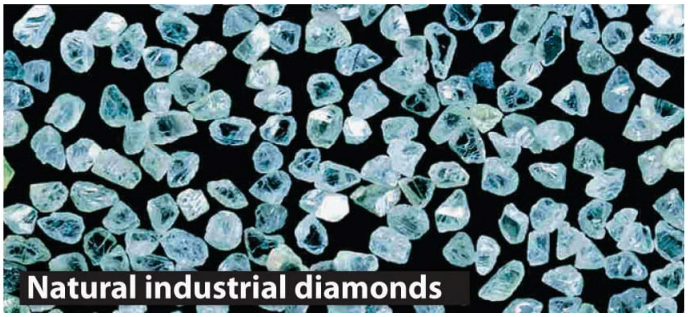
$$4B(s) + 3O_2(g) \xrightarrow{\Delta} 2B_2O_3(s) \tag{22.11.7}$$

$$2B(s) + 3X_2(g) \xrightarrow{\Delta} 2BX_3(g) \tag{22.11.8}$$

As is typical of elements lying near the dividing line between metals and nonmetals, many compounds of boron are amphoteric, dissolving in either acid or base.

Boron nitride is similar in many ways to elemental carbon. With eight electrons, the B–N unit is isoelectronic with the C–C unit, and B and N have the same average size and electronegativity as C. The most stable form of BN is similar to graphite, containing six-membered B_3N_3 rings arranged in layers. At high temperature and pressure, hexagonal BN converts to a cubic structure similar to diamond, which is one of the hardest substances known. Boron oxide (B_2O_3) contains layers of trigonal planar BO_3 groups (analogous to BX_3) in which the oxygen atoms bridge two boron atoms. It dissolves many metal and nonmetal oxides, including SiO_2, to give a wide range of commercially important borosilicate glasses. A small amount of CoO gives the deep blue color characteristic of “cobalt blue” glass.





At high temperatures, boron also reacts with virtually all metals to give metal borides that contain regular three-dimensional networks, or clusters, of boron atoms. The structures of two metal borides—ScB_{12} and CaB_6—are shown in Figure 22.11.4. Because metal-rich borides such as ZrB_2 and TiB_2 are hard and corrosion resistant even at high temperatures, they are used in applications such as turbine blades and rocket nozzles.

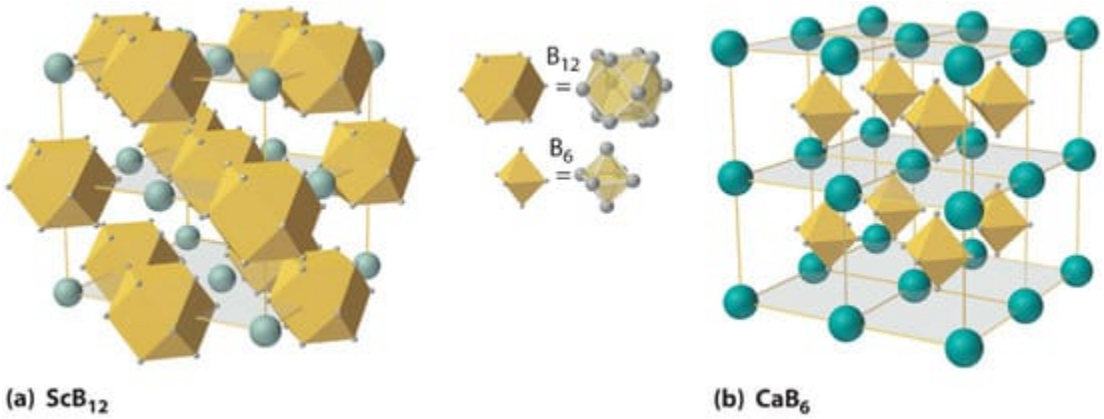


Figure 22.11.4: The Structures of $ScB_{12}$and CaB_6, Two Boron-Rich Metal Borides. *(a) The structure of ScB_{12} consists of B_{12} clusters and Sc atoms arranged in a faced-centered cubic lattice similar to that of NaCl, with B_{12}units occupying the anion positions and scandium atoms the cation positions. The B12 units here are not icosahedra but cubooctahedra, with alternating square and triangular faces. (b) The structure of CaB_6 consists of octahedral B_6 clusters and calcium atoms arranged in a body-centered cubic lattice similar to that of CsCl, with B_6 units occupying the anion positions and calcium atoms the cation positions.*

Boron hydrides were not discovered until the early 20th century, when the German chemist Alfred Stock undertook a systematic investigation of the binary compounds of boron and hydrogen, although binary hydrides of carbon, nitrogen, oxygen, and fluorine have been known since the 18th century. Between 1912 and 1936, Stock oversaw the preparation of a series of boron–hydrogen compounds with unprecedented structures that could not be explained with simple bonding theories. All these compounds contain multicenter bonds. The simplest example is diborane (B_2H_6), which contains two bridging hydrogen atoms (part (a) in Figure 22.11.5. An extraordinary variety of polyhedral boron–hydrogen clusters is now known; one example is the $B_{12}H_{12}^{2-}$ ion, which has a polyhedral structure similar to the icosahedral B_{12} unit of elemental boron, with a single hydrogen atom bonded to each boron atom.

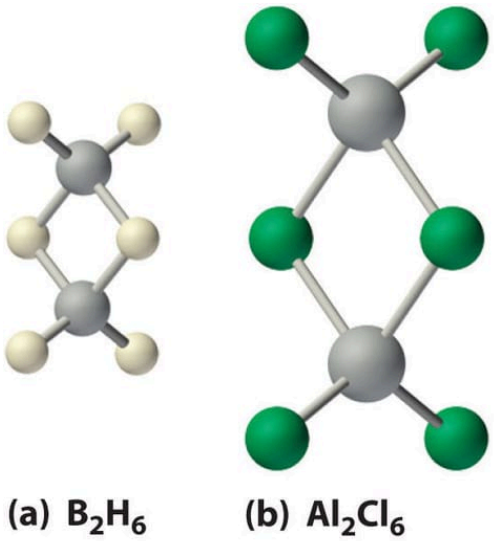
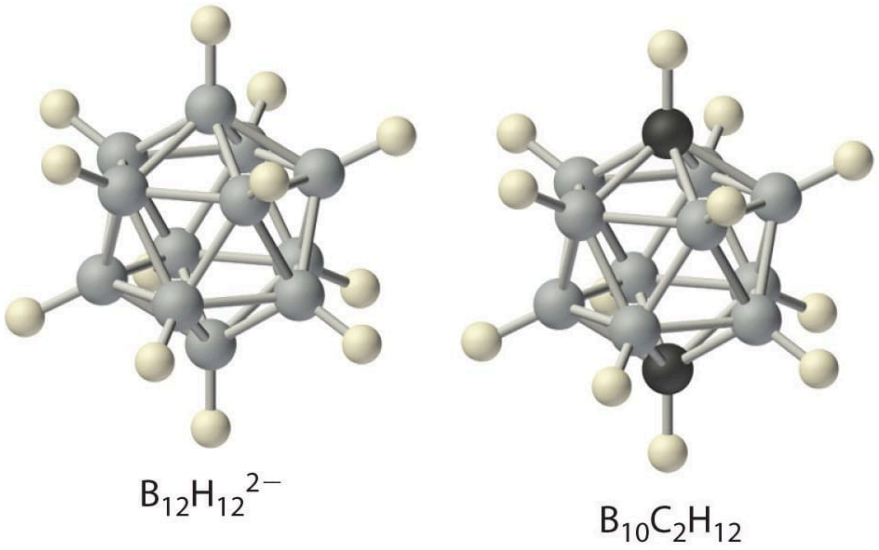


Figure 22.11.5: The Structures of Diborane (B_2H_6) and Aluminum Chloride (Al_2Cl_6). (a) The hydrogen-bridged dimer B_2H_6 contains two three-center, two-electron bonds as described for the $B_2H_7^-$ ion in Figure 21.5. (b) In contrast, the bonding in the halogen-bridged dimer Al_2Cl_6 can be described in terms of electron-pair bonds, in which a chlorine atom bonded to one aluminum atom acts as a Lewis base by donating a lone pair of electrons to another aluminum atom, which acts as a Lewis acid.

A related class of polyhedral clusters, the carboranes, contain both CH and BH units; an example is shown here. Replacing the hydrogen atoms bonded to carbon with organic groups produces substances with novel properties, some of which are currently being investigated for their use as liquid crystals and in cancer chemotherapy.



The enthalpy of combustion of diborane (B_2H_6) is –2165 kJ/mol, one of the highest values known:

$$B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(s)} + 3H_2O(l) \qquad \Delta H_{comb} = -2165\ kJ/mol \tag{22.11.9}$$

Consequently, the US military explored using boron hydrides as rocket fuels in the 1950s and 1960s. This effort was eventually abandoned because boron hydrides are unstable, costly, and toxic, and, most important, B_2O_3 proved to be highly abrasive to rocket nozzles. Reactions carried out during this investigation, however, showed that boron hydrides exhibit unusual reactivity.

Because boron and hydrogen have almost identical electronegativities, the reactions of boron hydrides are dictated by minor differences in the distribution of electron density in a given compound. In general, two distinct types of reaction are observed:

electron-rich species such as the BH_4^- ion are reductants, whereas electron-deficient species such as B_2H_6 act as oxidants.

Example 22.11.1

For each reaction, explain why the given products form.

a. $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(l)$
b. $BCl_3(l) + 3H_2O(l) \rightarrow B(OH)_3(aq) + 3HCl(aq)$
c. $2BI_3(s) + 3H_2(g) \xrightarrow{\Delta} \frac{1}{6}B_{12}(s) + 6HI(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution

a. Molecular oxygen is an oxidant. If the other reactant is a potential reductant, we expect that a redox reaction will occur. Although B_2H_6 contains boron in its highest oxidation state (+3), it also contains hydrogen in the –1 oxidation state (the hydride ion). Because hydride is a strong reductant, a redox reaction will probably occur. We expect that H^- will be oxidized to H^+ and O_2 will be reduced to O^{2-}, but what are the actual products? A reasonable guess is B_2O_3 and H_2O, both stable compounds.
b. Neither BCl_3 nor water is a powerful oxidant or reductant, so a redox reaction is unlikely; a hydrolysis reaction is more probable. Nonmetal halides are acidic and react with water to form a solution of the hydrohalic acid and a nonmetal oxide or hydroxide. In this case, the most probable boron-containing product is boric acid [$B(OH)_3$].
c. We normally expect a boron trihalide to behave like a Lewis acid. In this case, however, the other reactant is elemental hydrogen, which usually acts as a reductant. The iodine atoms in BI_3 are in the lowest accessible oxidation state (–1), and boron is in the +3 oxidation state. Consequently, we can write a redox reaction in which hydrogen is oxidized and boron is reduced. Because compounds of boron in lower oxidation states are rare, we expect that boron will be reduced to elemental boron. The other product of the reaction must therefore be HI.

Exercise 22.11.1

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $B_2H_6(g) + H_2O(l) \xrightarrow{\Delta}$
b. $BBr_3(l) + O_2(g) \rightarrow$
c. $B_2O_3(s) + Ca(s) \xrightarrow{\Delta}$

Answer

a. $B_2H_6(g) + H_2O(l) \xrightarrow{\Delta} 2B(OH)_3(s) + 6H_2(g)$
b. $BBr_3(l) + O_2(g) \rightarrow \text{no reaction}$
c. $6B_2O_3(s) + 18Ca(s) \xrightarrow{\Delta} B_{12}(s) + 18CaO(s)$

Reactions and Compounds of the Heavier Group 13 Elements

All four of the heavier group 13 elements (Al, Ga, In, and Tl) react readily with the halogens to form compounds with a 1:3 stoichiometry:

$$2M_{(s)} + 3X_{2(s,l,g)} \rightarrow 2MX_{3(s)} \text{ or } M_2X_6 \tag{22.11.10}$$

The reaction of Tl with iodine is an exception: although the product has the stoichiometry TlI_3, it is not thallium(III) iodide, but rather a thallium(I) compound, the Tl^+ salt of the triiodide ion (I_3^-). This compound forms because iodine is not a powerful enough oxidant to oxidize thallium to the +3 oxidation state.

Of the halides, only the fluorides exhibit behavior typical of an ionic compound: they have high melting points (>950°C) and low solubility in nonpolar solvents. In contrast, the trichorides, tribromides, and triiodides of aluminum, gallium, and indium, as well as $TlCl_3$ and $TlBr_3$, are more covalent in character and form halogen-bridged dimers (part (b) in Figure 22.11.4). Although the structure of these dimers is similar to that of diborane (B_2H_6), the bonding can be described in terms of electron-pair bonds rather than the delocalized electron-deficient bonding found in diborane. Bridging halides are poor electron-pair donors, so the group 13 trihalides are potent Lewis acids that react readily with Lewis bases, such as amines, to form a Lewis acid–base adduct:

$$Al_2Cl_{6(soln)} + 2(CH_3)_3N_{(soln)} \rightarrow 2(CH_3)_3N : AlCl_{3(soln)} \tag{22.11.11}$$

In water, the halides of the group 13 metals hydrolyze to produce the metal hydroxide (\[M(OH)_3\]):

$$MX_{3(s)} + 3H_2O_{(l)} \rightarrow M(OH)_{3(s)} + 3HX_{(aq)} \tag{22.11.12}$$

In a related reaction, $Al_2(SO_4)_3$ is used to clarify drinking water by the precipitation of hydrated $Al(OH)_3$, which traps particulates. The halides of the heavier metals (In and Tl) are less reactive with water because of their lower charge-to-radius ratio. Instead of forming hydroxides, they dissolve to form the hydrated metal complex ions: $[M(H_2O)_6]^{3+}$.

Of the group 13 halides, only the fluorides behave as typical ionic compounds.

Like boron (Equation 22.11.7), all the heavier group 13 elements react with excess oxygen at elevated temperatures to give the trivalent oxide (M_2O_3), although Tl_2O_3 is unstable:

$$4\mathrm{M(s)} + 3\mathrm{O_2(g)} \xrightarrow{\Delta} 2\mathrm{M_2O_3(s)} \tag{22.11.13}$$

Aluminum oxide (Al_2O_3), also known as alumina, is a hard, high-melting-point, chemically inert insulator used as a ceramic and as an abrasive in sandpaper and toothpaste. Replacing a small number of Al^{3+} ions in crystalline alumina with Cr^{3+} ions forms the gemstone ruby, whereas replacing Al^{3+} with a mixture of Fe^{2+}, Fe^{3+}, and Ti^{4+} produces blue sapphires. The gallium oxide compound $MgGa_2O_4$ gives the brilliant green light familiar to anyone who has ever operated a xerographic copy machine. All the oxides dissolve in dilute acid, but Al_2O_3 and Ga_2O_3 are amphoteric, which is consistent with their location along the diagonal line of the periodic table, also dissolving in concentrated aqueous base to form solutions that contain $M(OH)_4^-$ ions.

Group 13 trihalides are potent Lewis acids that react with Lewis bases to form a Lewis acid–base adduct.

Aluminum, gallium, and indium also react with the other group 16 elements (chalcogens) to form chalcogenides with the stoichiometry M_2Y_3. However, because Tl(III) is too strong an oxidant to form a stable compound with electron-rich anions such as S^{2-}, Se^{2-}, and Te^{2-}, thallium forms only the thallium(I) chalcogenides with the stoichiometry Tl_2Y. Only aluminum, like boron, reacts directly with N_2 (at very high temperatures) to give AlN, which is used in transistors and microwave devices as a nontoxic heat sink because of its thermal stability; GaN and InN can be prepared using other methods. All the metals, again except Tl, also react with the heavier group 15 elements (pnicogens) to form the so-called III–V compounds, such as GaAs. These are semiconductors, whose electronic properties, such as their band gaps, differ from those that can be achieved using either pure or doped group 14 elements. For example, nitrogen- and phosphorus-doped gallium arsenide ($GaAs_{1-x-y}P_xN_y$) is used in the displays of calculators and digital watches.

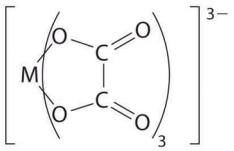
All group 13 oxides dissolve in dilute acid, but Al_2O_3 and Ga_2O_3 are amphoteric.

Unlike boron, the heavier group 13 elements do not react directly with hydrogen. Only the aluminum and gallium hydrides are known, but they must be prepared indirectly; AlH_3 is an insoluble, polymeric solid that is rapidly decomposed by water, whereas GaH_3 is unstable at room temperature.

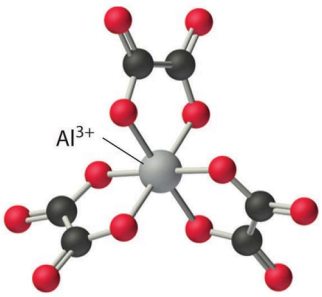
Complexes of Group 13 Elements

Boron has a relatively limited tendency to form complexes, but aluminum, gallium, indium, and, to some extent, thallium form many complexes. Some of the simplest are the hydrated metal ions $[M(H_2O)_6^{3+}]$, which are relatively strong Brønsted–Lowry acids that can lose a proton to form the $M(H_2O)_5(OH)^{2+}$ ion:

$$[M(H_2O)_6]^{3+}_{(aq)} \rightarrow M(H_2O)_5(OH)^{2+}_{(aq)} + H^+_{(aq)} \tag{22.11.14}$$



Oxalate ion



Al^{3+}–oxalate complex

Group 13 metal ions also form stable complexes with species that contain two or more negatively charged groups, such as the oxalate ion. The stability of such complexes increases as the number of coordinating groups provided by the ligand increases.

Example 22.11.2

For each reaction, explain why the given products form.

a. $2Al(s) + Fe_2O_3(s) \xrightarrow{\Delta} 2Fe(l) + Al_2O_3(s)$
b. $2Ga(s) + 6H_2O(l) + 2OH^-(aq) \xrightarrow{\Delta} 3H_2(g) + 2Ga(OH)_4^-(aq)$
c. $In_2Cl_6(s) \xrightarrow{H_2O(l)} 2In^{3+}(aq) + 6Cl^-(aq)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution

a. Aluminum is an active metal and a powerful reductant, and Fe_2O_3 contains Fe(III), a potential oxidant. Hence a redox reaction is probable, producing metallic Fe and Al_2O_3. Because Al is a main group element that lies above Fe, which is a transition element, it should be a more active metal than Fe. Thus the reaction should proceed to the right. In fact, this is the thermite reaction, which is so vigorous that it produces molten Fe and can be used for welding.

b. Gallium lies immediately below aluminum in the periodic table and is amphoteric, so it will dissolve in either acid or base to produce hydrogen gas. Because gallium is similar to aluminum in many of its properties, we predict that gallium will dissolve in the strong base.
c. The metallic character of the group 13 elements increases with increasing atomic number. Indium trichloride should therefore behave like a typical metal halide, dissolving in water to form the hydrated cation.

Exercise 22.11.2

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $LiH(s) + Al_2Cl_6(soln) \rightarrow$
b. $Al_2O_3(s) + OH^-(aq) \rightarrow$
c. $Al(s) + N_2(g) \xrightarrow{\Delta}$
d. $Ga_2Cl_6(soln) + Cl^-(soln) \rightarrow$

Answer

a. $8LiH(s) + Al_2Cl_6(soln) \rightarrow 2LiAlH_4(soln) + 6LiCl(s)$
b. $Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)$
c. $2Al(s) + N_2(g) \xrightarrow{\Delta} 2AlN(s)$
d. $Ga_2Cl_6(soln) + 2Cl^-(soln) \rightarrow 2GaCl_4^-(soln)$

Summary

Compounds of the group 13 elements with oxygen are thermodynamically stable. Many of the anomalous properties of the group 13 elements can be explained by the increase in Z_{eff} moving down the group. Isolation of the group 13 elements requires a large amount of energy because compounds of the group 13 elements with oxygen are thermodynamically stable. Boron behaves chemically like a nonmetal, whereas its heavier congeners exhibit metallic behavior. Many of the inconsistencies observed in the properties of the group 13 elements can be explained by the increase in Z_{eff} that arises from poor shielding of the nuclear charge by the filled $(n - 1)d^{10}$ and $(n - 2)f^{14}$ subshells. Instead of forming a metallic lattice with delocalized valence electrons, boron forms unique aggregates that contain multicenter bonds, including metal borides, in which boron is bonded to other boron atoms to form three-dimensional networks or clusters with regular geometric structures. All neutral compounds of the group 13 elements are electron deficient and behave like Lewis acids. The trivalent halides of the heavier elements form halogen-bridged dimers that contain electron-pair bonds, rather than the delocalized electron-deficient bonds characteristic of diborane. Their oxides dissolve in dilute acid, although the oxides of aluminum and gallium are amphoteric. None of the group 13 elements reacts directly with hydrogen, and the stability of the hydrides prepared by other routes decreases as we go down the group. In contrast to boron, the heavier group 13 elements form a large number of complexes in the +3 oxidation state.

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22.E: Chemistry of the Nonmetals (Exercises)

22.1: General Concepts: Periodic Trends and Reactions

22.2: Hydrogen

22.3: Group 18: Nobel Gases

Questions

1. The chemistry of the noble gases is largely dictated by a balance between two competing properties. What are these properties? How do they affect the reactivity of these elements?
2. Of the group 18 elements, only krypton, xenon, and radon form stable compounds with other atoms and then only with very electronegative elements. Why?
3. Give the type of hybrid orbitals used by xenon in each species.

    a. XeF_2
    b. XeF_4
    c. XeO_3
    d. $XeOF_4$
    e. XeO_4
    f. XeO_6^{4-}

4. Which element is the least metallic—B, Ga, Tl, Pb, Ne, or Ge?
5. Of Br, N, Ar, Bi, Se, He, and S, which would you expect to form positive ions most easily? negative ions most easily?
6. Of BCl_3, BCl_4^-, CH_4, $H_3N{\cdot}BF_3$, PCl_3, PCl_5, XeO_3, H_2O, and F^-, which species do you expect to be

    a. electron donors?
    b. electron acceptors?
    c. neither electron donors nor acceptors?
    d. both electron donors and acceptors?

7. Of HCl, $HClO_4$, HBr, H_2S, HF, KrF_2, and PH_3, which is the strongest acid?
8. Of CF_4, NH_3, NF_3, H_2O, OF_2, SiF_4, H_2S, XeF_4, and SiH_4, which is the strongest base?

Structure and Reactivity

1. Write a balanced chemical equation showing how you would prepare each compound from its elements and other common compounds.
    a. XeF_2
    b. XeF_4
    c. XeF_6
    d. $XeOF_4$
    e. XeO_3

2. Write a balanced chemical equation showing how you would make each compound.
    a. XeF_2 from Xe gas
    b. $NaXeF_7$ from its elements
    c. RnO_3 from Rn

3. In an effort to synthesize XeF_6, a chemist passed fluorine gas through a glass tube containing xenon gas. However, the product was not the one expected. What was the actual product?
4. Write a balanced chemical equation to describe the reaction of each species with water.

    a. B_2H_6
    b. F_2
    c. C^{4+}

5. Using heavy water (D_2O) as the source of deuterium, how could you prepare each compound?
    a. $LiAlD_4$
    b. D_2SO_4
    c. SiD_4
    d. DF

6. Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

    a. $Al_2O_3(s)$ in $OH^-(aq)$
    b. $Ar(g) + F_2(g)$
    c. $PI_3(s) + H_2O(l)$
    d. $H_3PO_3(l) + OH^-(aq)$
    e. $Bi(s)$ + excess $Br_2(l)$

Answers

a. $Xe(g) + F_2(g) \rightarrow XeF_2(s)$
b. $Xe(g) + 2F_2(g) \rightarrow XeF_4(s)$
c. $Xe(g) + 3F_2(g) \rightarrow XeF_6(s)$
d. $2XeF_6(s) + SiO_2(s) \rightarrow 2XeOF_4(l) + SiF_4(l)$
e. $XeF_6(s) + 3H_2O(l) \rightarrow XeO_3(s) + 6HF(aq)$

3. SiF_4; $SiO_2(s) + 2F_2(g) \rightarrow SiF_4(l) + 2O_2(g)$

5. a. $2Na(s) + 2D_2O(l) \rightarrow D_2(g) + 2NaOD(aq)$

    $2Li(s) + D_2(g) \rightarrow 2LiD(s)$

    $4LiD(s) + AlCl_3(soln) \rightarrow LiAlD_4(s) + 3LiCl(soln)$

    b. $D_2O(l) + SO_3(g) \rightarrow D_2SO_4(l)$
    c. $SiCl_4(l) + LiAlD_4(s)$ [from part (a)] $\rightarrow SiD_4(g) + LiCl(s) + AlCl_3(s)$
    d. $CaF_2(s) + D_2SO_4(l)$ [from part (b)] $\rightarrow 2DF(g) + CaSO_4(s)$

22.4: Group 7A: The Halogens

Questions

1. The lightest elements of groups 15, 16, and 17 form unusually weak single bonds. Why are their bonds so weak?
2. Fluorine has an anomalously low F–F bond energy. Why? Why does fluorine form compounds only in the –1 oxidation state, whereas the other halogens exist in multiple oxidation states?
3. Compare AlI_3, $InCl_3$, GaF_3, and $LaBr_3$ with respect to the type of M–X bond formed, melting point, and solubility in nonpolar solvents.
4. What are the formulas of the interhalogen compounds that will most likely contain the following species in the indicated oxidation states: I (+3), Cl (+3), I (–1), Br (+5)?
5. Consider this series of bromides: $AlBr_3$, $SiBr_4$, and PBr_5. Does the ionic character of the bond between the Br atoms and the

central atom decrease or increase in this series?

6. Chromium forms compounds in the +6, +3, and +2 oxidation states. Which halogen would you use to produce each oxidation state? Justify your selections.
7. Of ClF_7, BrF_5, IF_7, BrF_3, ICl_3, IF_3, and IF_5, which one is least likely to exist? Justify your selection.

Answers

1. Electrostatic repulsions between lone pairs on adjacent atoms decrease bond strength.

5. Ionic character decreases as $\Delta\chi$ decreases from Al to P.

7. ClF_7

Structure and Reactivity

1. SiF_4 reacts easily with NaF to form SiF_6^{2-}. In contrast, CF_4 is totally inert and shows no tendency to form CF_6^{2-} under even extreme conditions. Explain this difference.
2. Predict the products of each reaction and then balance each chemical equation.

    a. $Xe(g) + \text{excess } F_2(g) \rightarrow$
    b. $Se(s) + Cl_2(g) \rightarrow$
    c. $SO_2(g) + Br_2(g) \rightarrow$
    d. $NaBH_4(s) + BF_3(soln) \rightarrow$

3. Write a balanced chemical equation for the reaction of aqueous HF with
    a. SiO_2.
    b. Na_2CO_3.
    c. CaO.

4. Oxyhalides of sulfur, such as the thionyl halides (SOX_2, where X is F, Cl, or Br), are well known. Because the thionyl halides react vigorously with trace amounts of water, they are used for dehydrating hydrated metal salts. Write a balanced chemical equation to show the products of reaction of $SOCl_2$ with water.

5. Write a balanced chemical equation describing each reaction.
    a. the burning of sulfur in a chlorine atmosphere
    b. the dissolution of iodine in a potassium iodide solution
    c. the hydrolysis of PCl_3
    d. the preparation of HF from calcium fluoride and sulfuric acid
    e. the thermal decomposition of $KClO_3$
    f. the oxidation of sulfide ion by elemental iodine

6. Write the complete Lewis electron structure, the type of hybrid used by the central atom, and the number of lone pair electrons present on the central atom for each compound.
    a. CF_4
    b. PCl_3
    c. XeF_4

Answers

1. Carbon has no low energy d orbitals that can be used to form a set of d^2sp^3 hybrid orbitals. It is also so small that it is impossible for six fluorine atoms to fit around it at a distance that would allow for formation of strong C–F bonds.
3.

    a. $SiO_2(s) + 6HF(aq) \rightarrow SiF_6^{2-}(aq) + 2H^+(aq) + 2H_2O(l)$
    b. $Na_2CO_3(s) + 2HF(aq) \rightarrow CO_2(g) + 2NaF(aq) + H_2O(l)$

c. $CaO(s) + 2HF(aq) \rightarrow CaF_2(s) + H_2O(l)$

5.

a. $S_8(s) + 4Cl_2(g) \rightarrow 4S_2Cl_2(l)$
b. $I_2(s) + KI(aq) \rightarrow I_3^-(aq) + K^+(aq)$
c. $PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$
d. $CaF_2(s) + H_2SO_4(aq) \rightarrow 2HF(aq) + CaSO_4(s)$
e. $2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$
f. $8S^{2-}(aq) + 8I_2(aq) \rightarrow S_8(s) + 16I^-(aq)$

22.5: Oxygen

22.6: The Other Group 6A Elements: S, Se, Te, and Po

22.7: Nitrogen

Problems

- Complete and balance the following equations

  N_2 + ___H_2 → ___NH_

  $H_2N_2O_2 \rightarrow$?

  $2NH_3 + CO_2 \rightarrow$?

  _Mg + $N_2 \rightarrow$ Mg_N_

  $N_2H_5 + H_2O \rightarrow$?

- What are the different isotopes of Nitrogen?
- List the oxiadation states of various nitrogen oxides: N_2O, NO, N_2O_3, N_2O_4, N_2O_5
- List the different elements that Nitrogen will react with to make it basic or acidic....
- Uses of nitrogen

Answers

- Complete and balance the following equations

  $N_2 + 3H_2 \rightarrow 2NH_3$(Haber process)

  $H_2N_2O_2 \rightarrow HNO$

  $2NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O$

  $2Mg + 3N_2 \rightarrow Mg_3N_2$

  $N_2H_5 + H_2O \rightarrow N_2 + H^+ + H_2O$

- What are the different isotopes of Nitrogen?

Stable forms include nitrogen-14 and nitrogen-15

- List the oxidation states of various nitrogen oxides: +1, +2, +3, +4, +5 respectively
- List the different elements that Nitrogen will react with to make it basic or acidic :Nitride ion is a strong base when reacted with water, Ammonia is generally a weak acid
- Uses of nitrogen include anesthetic, Refrigerant, metal protector

22.8: The Other Group 5A Elements: P, AS, Sb, and Bi

22.9: Carbon

22.10: The Other Group 4A Elements: Si, Ge, Sn, and Pb

22.11: Boron

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22.S: Chemistry of the Nonmetals (Summary)

Descriptive chemistry of the elements is consistent with the various principles discussed earlier. We will focus on trends in and explanations for the observed behavior of the elements.

22.1: General Concepts: Periodic Trends and Reactions

Main group elements -- the valence electrons are filling s and p orbitals

- Three types of main-group elements: metal, metalloid, nonmetal
- Increasing metallic character going down a group and from right to left across a period
- Group Work: List the relative properties of the metals:
- volatility
- melting and boiling points
- density
- thermal conductance
- electrical conductance
- appearance as solids
- brittleness
- typical structure
- bonding
- tendency to lose or gain electrons
- acidity/basicity of oxides

Metals

Metals are nonvolatile, high melting and boiling points, high density and thermal and electrical conductance, characteristic shine or luster as crystalline solids, malleable and ductile, consist of large arrays of atoms with long-range bonding forces (the metallic bond) between free electrons and cations, tend to lose electrons, oxides are alkaline

- Group Work: List the relative properties of the non-metals:
- volatility
- melting and boiling points
- density
- thermal conductance
- electrical conductance
- appearance as solids
- brittleness
- typical structure
- bonding
- tendency to lose or gain electrons
- acidity/basicity of oxides

NonMetals

Nonmetals are volatile, low melting and boiling points, low density, brittle or soft as solids, low thermal and electrical conductance, solids dull in appearance, many are discrete small molecules with atoms joined by strong covalent bonds, intermolecular forces between molecules are weak, chemical properties characterized by their tendency to gain electrons, oxides are usually acidic

- Group Work: Which group of metals is the most reactive?
- Alkali metals - why?
- Which group of nonmetals is the most reactive?
- Halogens - why?
- Compare the metalloids to the metals and the non-metals.

Metalloids

- Metalloids: physical properties more like those of metals, but chemical reactivity is more like that of nonmetals; many atomic properties are intermediate between those of metals and of nonmetals Period 2 Elements are Unique
- Compounds formed between nonmetals tend to be molecular.
- As we move down the periodic table bonding changes.
- The third period onwards has accessible d-orbitals that can participate in bonding.
- Therefore, the octet rule can be broken for the third period onwards.
- The first member of a group can form π bonds more readily than subsequent members.
- Si is much larger than C and the 3p orbital is much larger than the 2p orbital, so the overlap between 3p orbitals to form a π3p bond is significantly poorer than for a π2p bond.
- Since the Si-Si π bond is much weaker than the C-C π bond, Si tends to form σ bonds.
- Example: CO2 is a gas with O=C=O bonds. SiO2 is a network solid with Si-O bonds.

Lightest Elements are Unique

- Properties of the first element in each group are usually more distinctive, while the rest of the elements in a group have similar properties
- The unusual properties of the first element in a group can be explained on the basis of its unusually small size, which arises because the valence electrons are not shielded from the nucleus and the electrons are held relatively tightly in the atom Metals with Covalent Bonds
- Small metal ions such as Be2+ are polarizing and pull electrons from nonmetal anions to form partly covalent bonds.
- Small nonmetals (such as N, O, F) are highly electronegative because of the increased attraction of the nucleus for the electrons at short distances and form multiple bonds because p orbitals can overlap. Chapter 22 22-3

Diagonal Relationships

In addition to horizontal and vertical trends, there is a diagonal relationship between elements such as Li and Mg, Be and Al, B and Si, that have an adjacent upper left/lower right relative location in the periodic table.

- These pairs of elements have similar size and electronegativity, resulting in similar properties. 22.2 Hydrogen Isotopes of Hydrogen
- There are three isotopes of hydrogen: Protium 1 1H, deuterium 2 1H, and tritium 3 1H.
- Deuterium (D) is about 0.0156 % of naturally occurring H.
- Tritium (T) is radioactive with a half-life of 12.3 yr.

22.2: Hydrogen

- Hydrogen is unique.
- Hydrogen has a 1s1 electron configuration so it is placed above Li in the periodic table.
- However, H is significantly less reactive than the alkali metals.
- Hydrogen can gain an electron to form H- , which has a He electron configuration. Therefore, H could be placed above the halogens.
- However, the electron affinity of H is lower than any halogen.
- Elemental hydrogen is a colorless, odorless gas at room temperature.
- Since H2 is nonpolar and only has two electrons, the intermolecular forces are weak (boiling point -253°C, melting point -259°C).
- The H-H bond enthalpy is high (436 kJ/mol). Therefore, reactions with hydrogen are slow and a catalyst needs to be used.
- When hydrogen reacts with air explosions result (Hindenburg exploded in 1937):

$$2H2(g) + O2(g) \rightarrow 2H2O(l)$$

with $\Delta H = -571.7\ kJ/mol$

Preparation of Hydrogen

- In the laboratory hydrogen is usually prepared by reduction of an acid.
- Zn is added to an acidic solution and hydrogen bubbles are formed.
- The hydrogen bubbles out of solution and is collected in a flask.
- The collection flask is usually filled with water so the volume of hydrogen collected is the volume of water displaced.

In larger quantities, hydrogen can be prepared by the reduction of methane in the presence of steam at 1100°C:

$$CH4(g) + H2O(g) \rightarrow CO(g) + 3H2(g)$$

$$CO(g) + H2O(g) \rightarrow CO2(g) + H2(g)$$

Uses of Hydrogen

- Hydrogen is used for ammonia production and to hydrogenate vegetable oils to make margarine and shortening.
- Hydrogen is used to manufacture methanol: [CO(g) + 2H2(g) → CH3OH(g) \nonumber \]
- Chapter 22

Binary Hydrogen Compounds

- There types of binary hydrogen compounds are formed:
- ionic hydrides (e.g. LiH, made between metals and H);
- metallic hydrides (e.g. TiH2, made between transition metals and H); and
- molecular hydrides (e.g. CH4, made between nonmetals and metalloids and H).
- Thermal stability (measured by ΔG°f) decreases as we go down a group and increases across a period.
- Most stable is HF.
- Metal hydrides, such as CaH2, react with water to give H2 and metal hydroxide.

22.3: Group 18: Nobel Gases

- Noble gases are very unreactive.
- All elements have high ionization energies.
- He is the most important noble gas as liquid helium is used as a coolant.
- The heavier noble gases react more readily than the lighter ones.
- The most common compounds of noble gases are xenon fluorides.
- Xenon fluorides have Xe in the +2 to +8 oxidation states.
- Noble gas compounds violate the octet rule.
- In the presence of water, xenon fluorides form oxyfluorides:
- XeF6(s) + H2O(l) → XeOF4(l) + 2HF
- XeF6(s) + 3H2O(l) → XeO3(aq) + 6HF
- The only other noble gas compound known is KrF2, which decomposes at -10°C.
- Xenon fluorides are more stable than the oxides and oxyfluorides.

22.4: Group 17: The Halogens

- F, Cl, Br, I, At
- Most common are chlorine, bromine, and iodine
- Fluorine has properties atypical of the group
- Astatine is radioactive and exists naturally only in very small amounts
- The halogens exist as diatomic molecules
- At room temperature, fluorine is a yellow gas, chlorine is a pale green gas, bromine is a red liquid, and iodine is a purple solid
- The elements have very high ionization energies, typical of nonmetals

Properties of the Halogens

Outer electron configurations: ns2np5.

All halogens have large electron affinities.

Most common oxidation state is -1, but oxidation states of +1, +3, +5 and +7 are possible.

Halogens are good oxidizing agents.

Each halogen is the most electronegative element in its row.

The properties of the halogens vary regularly with their atomic number. Chapter 22 22-5 Fluorine

The bond enthalpy of F2 is low. Hence fluorine is very reactive.

Water is oxidized more readily than fluorine, so F2 cannot be prepared by electrolysis of a salt solution. F2 is an extremely reactive gas, which reacts with all the elements, except oxygen and the lighter noble gases, to form stable fluorides, often explosively.

F2 is such a strong oxidizing agent that it can convert oxides, including water, to molecular oxygen

Write a balanced equation for the reaction of F2 with H2O (to form O2 and ??).

Chlorine

- Chlorine exists as chlorides in sea water, salt lakes, and brine deposits
- Cl2 gas prepared industrially by the electrolysis of sodium chloride solutions
- Also a by-product of the preparation of metals by electrolysis of molten salts such as NaCl, MgCl2, and CaCl2
- Most Cl2 is used as a raw material in the production of other chemicals, in the synthesis of herbicides and insecticides, in the bleaching of textiles and paper, in purifying drinking water, and in the production of plastics such as polyvinyl chloride (PVC)

Bromine

- Bromine exists in small quantities in the form of bromides co-existing with chlorides
- Prepared by reacting a solution containing bromide ion with chlorine
- Uses of bromine:
- as a bleach
- in the manufacture of bromide compounds
- ethylene bromide, $C_2H_4Br_2$, used as an antiknock agent in gasoline

Iodine

- Iodine exists as iodides in brines and seaweed, and as iodates in deposits of sodium nitrate (NaNO3, or Chile saltpeter)
- Recovered by oxidation of I- with Cl2 or by reduction of IO3 - with HSO3 -
- Used as an antiseptic and disinfectant and as a reagent for chemical analysis

Astatine

- Not much is known about its chemistry
- It is highly radioactive; all chemical studies have used small quantities added to iodine solutions and measure behavior by determining where the radioactivity ends up.
- The total amount in the Earth's crust is estimated to be < 30 g at any one time.

Halogens

- In addition to the common -1 and 0 oxidation numbers, the halogens (except for fluorine) exist with each positive oxidation number through +7
- Halogen oxides are known with oxidation numbers as high as +7; most are very strong oxidizing agents

22-6 Oxyacids and Oxyanions

- Fluorine only forms one oxyacid: HOF. Oxygen is in the zero oxidation state.
- All are strong oxidizing agents.
- All are unstable and decompose readily.
- Oxyanions are more stable than oxyacids.
- Acid strength increases as the oxidation state of the halogen increases.

Periodic Acid

- Periodic (HIO4) and paraperiodic (H5IO6) acid have iodine in the +7 oxidation state.
- Periodic acid is a strong acid, paraperiodic acid is a weak acid (Ka1 = 2.8 × 10-2, Ka2 = 4.9 × 10-9).
- The large iodine atom allows 6 oxygen atoms around it.
- Smaller halogens cannot form this type of compound.

Halogens

Many aqueous halogen species are susceptible to disproportionation:

- ClO2
- HClO2
- HOCl
- Cl2 (in base)
- HOBr
- Br2 (in base)
- HOI
- IO-
- I2 (in base)

How do we decide which species will disproportionate?

22.5: Oxygen

Properties of Oxygen

- Oxygen has two allotropes: O2 and O3.
- O2 is a colorless, odorless gas at room temperature.
- The electron configuration is [He]2s2 2p4 , which means the dominant oxidation state is 2-.
- The O=O bond is strong (bond enthalpy 495 kJ/mol). Preparation of Oxygen
- Commercially: obtained by fractional distillation of air. (Normal boiling point of O2 is -183°C and N2 -196°C.)
- Laboratory preparation of oxygen is the catalytic decomposition of KClO3 in the presence of

$$MnO2 : 2KClO3(s) \rightarrow 2KCl(s) + 3O2(g).$$

- Atmospheric oxygen is replenished by photosynthesis (process in plants where CO2 is converted to O2 in the presence of sunlight).

Uses of Oxygen

- Most widely used as an oxidizing agent. (E.g. in the steel industry to remove impurities.)
- Oxygen is used in medicine.
- It is used with acetylene, C2H2 for oxyacetylene welding:

$$2C2H2(g) + 5O2(g) \rightarrow 4CO2(g) + 2H2O(g)$$

Ozone

- Pale blue, poisonous gas.
- Ozone dissociates to form oxygen: O3(g) → O2(g) + O(g) ΔH° = 107 kJ
- Ozone is a stronger oxidizing agent than oxygen: O3(g) + 2H+ (aq) + 2e- → O2(g) + H2O(l) E° = 2.07 V O2(g) + 4H+ (aq) + 4e- → 2H2O(l) E° = 1.23 V
- Ozone can be made by passing an electric current through dry O2: 3O2(g) → 2O3(g)

Peroxides and Superoxides

- Peroxides: have an O-O bond and O in the -1 oxidation state.
- Hydrogen peroxide is unstable and decomposes into water and oxygen: 2H2O2(l) → 2H2O(l) + O2(g) ΔH = -196.0 kJ
- The oxygen produced will kill bacteria.
- Peroxides are important in biochemistry: it is produced when O2 is metabolized.

Peroxides

- Disproportionation occurs when an element is simultaneous oxidized and reduced: 2H+ (aq) + H2O2(aq) + 2e- → 2H2O(l) E° = 1.78 V O2(g) + 2H+ (aq) + 2e- → H2O2(aq) E° = 0.68 V
- Disproportionation: 2H2O2(aq) → 2H2O(l) + O2(g) E° = 1.10 V

Superoxides

- Superoxides: have an O-O bond and O in an oxidation state of -½ (superoxide ion is O2-).
- Usually form with active metals (KO2, RbO2 and CsO2).
- Potassium superoxide reacts with water vapor from the breath to form oxygen gas. 4KO2 + 2H2O → 3O2 + 4KOH 22.6 The Other Group 6A Elements: S, Se, Te, and Po (Chalcogens)
- Trend that affects other properties is the increase in metallic character down the group, indicated by the decreases in ionization energy and electronegativity

22.6: The Other Group 16 Elements: S, Se, Te, and Po

- Nonmetallic character dominates in this group
- Nonmetallic O exists as diatomic molecules
- Nonmetallic S exists as various covalently bonded polyatomic forms
- Metalloids Se and Te are more metallic than S, but bear some resemblance to S
- Po is even more metallic, but its behavior is not well known since it is a rare, radioactive element
- Oxygen dominated by oxidation number -2
- The other elements have oxidation numbers from -2 through +6, the higher ones being quite common, especially in combination with oxygen

Sulfur

- S found in earth's crust as sulfide and sulfate minerals and as the free element
- Also a small but critical constituent of plant and animal tissue
- Occurs as sulfur dioxide and sulfur trioxide in the atmosphere
- Elemental sulfur is a tasteless, odorless, combustible yellow solid existing in a variety of allotropes with different molecular

structures
- Rhombic and monoclinic forms consist of S8 rings
- Major use of sulfur is the preparation of sulfuric acid, which is used primarily to make phosphate fertilizers and impure phosphoric acid from phosphate rock
- Sulfur forms binary compounds with all the elements except iodine and the noble gases
- Hydrogen sulfide (H2S):
- usually prepared by reaction of a metal sulfide with an acid
- gas well known for its "rotten-egg" odor
- extremely poisonous
- largest source of sulfur in the atmosphere
- Sulfur reacts with oxygen to form two oxides, sulfur dioxide and sulfur trioxide, which form oxoanions (SO3 2- and SO4 2-) and oxoacids (H2SO3 and H2SO4) by reaction with metal oxides or water
- Sulfuric acid is a powerful dehydrating agent, strong acid and moderate oxidizer.
- Sulfuric acid removes H2O from the sugar leaving a black mass of C. Steam is produced because the reaction is very exothermic.

Exercise $22.S.1$

What are the structures of:

- SO2
- SO3
- SO3 2-
- SO4 2-
- H2SO3
- H2SO4

22.7: Nitrogen

- Electronic configuration of the Group VA (15) elements is ns2 np3
- Little resemblance between the chemistry of nitrogen and the other elements in this group Chapter

Nitrogen

- Nitrogen as an element is the colorless, odorless, diatomic molecule N2, the major constituent of air
- An essential component of all living matter in protein and amino acids
- Nitrogen compounds are important components of chemical fertilizers
- Most uses of nitrogen involve its compounds, such as ammonia and nitrogen oxides.

Exercise $22.S.2$

- List the formulas for all the oxides that you expect nitrogen to form.

Preparation of Nitrogen

- N2 is produced by fractional distillation of air.
- Nitrogen is fixed by forming NH3 (Haber Process).
- NH3 is converted into other useful chemicals (NO, NO2, nitrites and nitrates).

Nitrogen

- Positive oxidation numbers of nitrogen occur in the oxides, including N2O, NO, N2O3, NO2, N2O4, and N2O5.

- Aqueous N_2O_3 is converted to nitrous acid (HNO_2), and N_2O_5 to nitric acid (HNO_3).
- Nitrous oxide, N_2O, occurs naturally in the atmosphere, as a result of the natural degradation of proteins.
- N_2O can be formed by thermal decomposition of NH_4NO_3
- N_2O is used as an anesthetic (in laughing gas)
- Nitric oxide, NO, is formed by reaction of Cu metal with dilute aqueous nitric acid or in high temperature combustion processes and in the oxidation of ammonia gas commercially
- NO reacts rapidly with O_2 to form reddish-brown NO_2.
- Dinitrogen trioxide results from reaction between NO and NO_2.
- N_2O_3 is blue as a liquid.
- Gaseous N_2O_3 reacts with water to form the weak acid, nitrous acid, HNO_2.

Exercise $22.S.3$

- Write an equation for the preparation of nitrogen dioxide from common laboratory chemicals.

Nitrogen

- Nitrogen dioxide, NO_2, is a poisonous, reddish-brown gas with an irritating odor, which exists in equilibrium with colorless N_2O_4
- Dinitrogen pentoxide, N_2O_5, is a volatile low-melting white solid; dissolved in water, it forms HNO_3, nitric acid

22.8: The Other Group 15 Elements: P, AS, Sb, and Bi

- Although nitrogen is found in nature primarily as unreactive N_2, the other elements are found only in compounds
- Metallic nature increases down the group

Exercise $22.S.43$

Predict the following properties for phosphorus:

- metallic character
- type of bonding
- acid/base character of oxides
- formulas of oxides Phosphorus

- Phosphorus is essentially nonmetallic, forms covalent bonds and has acidic oxides Group Work
- Predict the acid/base character of the oxides of As, Sb, and Bi, relative to those of P. How can we explain the predicted trend? Group 5A
- Arsenic has properties between those of a nonmetal and a metalloid, with amphoteric (though more acidic than basic) oxides
- Antimony is mostly metallic, but with some properties of a metalloid, and amphoteric (more basic than acidic) oxides
- Bismuth, is metallic, with basic oxides
- These trends are consistent with dramatic decreases in ionization energy down the group
- Trends in oxidation number:
- N and P range from -3 to +5
- As primarily +3 and +5
- Sb mostly +3, occasionally +5
- Bi almost exclusively +3, rarely as +5
- The lower, more metallic elements in the group have fewer stable oxidation numbers than N

Phosphorus

- Phosphorus found as phosphates in 190 different minerals, most importantly apatite, $Ca_5(PO_4)_3OH$
- Phosphates are an important constituent of all bone tissue
- Mainly occurs in phosphorus minerals (e.g. phosphate rock, $Ca_3(PO_4)_2$).

- Elemental P4 produced by reduction

$$2Ca3(PO4)2(s) + 6SiO2(s) + 10C(s) \rightarrow P4(g) + 6CaSiO3(l) + 10CO(g)$$

- Phosphoric acid, made from phosphate rock, is one of the ingredients in Coca-Cola.
- Phosphorus occurs as 19 allotropes, the principal ones being white (tetrahedral P4), red, and black phosphorus
- White phosphorus is a soft solid, with molecules held together by weak intermolecular forces.
- White phosphorus is poisonous and causes painful skin burns.
- White phosphorus is quite reactive and ignites spontaneously in air
- Red phosphorus is an amorphous solid formed by heating white phosphorus
- Red phosphorus involves P4 tetrahedral molecules bonded to one another in long chains
- Black phosphorus is still less reactive
- Black phosphorus may be amorphous or have a graphite-like structure; it is metallic in appearance and an electrical conductor

Exercise $22.S.1$

What acids are formed when the oxides, P4O6 and P4O10, are reacted with excess water?

Phosphorus

- Two oxides of phosphorus, P4O6 and P4O10, formed by burning phosphorus
- React with water to form phosphorous acid, H3PO3 and phosphoric acid, H3PO4
- P4O10 is used as a drying agent because of its affinity for water. 22.9 Carbon
- Carbon constitutes about 0.027 % of the earthís crust.
- Carbon is the main constituent of living matter.
- Study of carbon compounds is called organic chemistry.
- Carbon forms more compounds than all other elements except hydrogen; typical compounds are the hydrocarbons and their derivatives
- Exists as diamond, graphite, and an amorphous form, as well as the recently discovered allotrope C60, called buckminsterfullerene
- Diamond: clear crystalline form of carbon, one of the hardest substances known, can be synthesized from graphite with high temperature and pressure and a metal catalyst

Exercise $22.S.1$

Why is diamond so hard, while graphite is soft and slippery, even though both are pure carbon?

22.9: Carbon

- Graphite:
  - slippery gray-black solid
  - strong covalent bonds hold atoms together in each layer, but the layers are bonded only by weak van der Waals forces, so the layers slide across one another readily
  - found widely distributed in the earth's crust and synthesized from amorphous carbon
- Uses of graphite:
  - crucibles
  - lubricants
  - pencils
  - nuclear reactors (to slow down fast neutrons)
  - electrodes for electrolysis reactions
- Amorphous carbon:
  - carbon blacks
  - charcoal
  - activated carbon

    - soot
    - coke
- Essentially microcrystalline forms of graphite with no layering
- Formed by thermal decomposition or partial decomposition of coal, petroleum, natural gas, and wood with an insufficient supply of oxygen
- burning oil gives lampblack
- heating coal in the absence of air produces coke
- heating wood in the absence of air gives charcoal
- Carbon black used as a filler in rubber tires to increase toughness and prevent brittleness
- Lampblack used in inks, paints, coating on carbon paper
- Charcoal used:
    - in filters to adsorb odors
    - in gas masks to adsorb poisonous gases
    - in the decolorizing of sugar
    - in water treatment
    - in the reclamation of dry-cleaning solvents
- Coke used in the extraction of metals from their oxide ores
- Buckminsterfullerene consists of molecules of C60 formed by laser or high- temperature carbon arc vaporization of graphite
- One member of a class of new forms of carbon called fullerenes, which consist of clusters of carbon atoms containing even numbers from 44 to 84
- C60 exists as a truncated icosahedron, which contains 12 pentagonal faces and 20 hexagonal faces
- Remarkable physical stability, but chemically reactive
- Now being prepared as tubes, into which metals can be inserted. These are the thinnest capillary tubes known.
- Elemental carbon is relatively unreactive at room temperature
- Insoluble in water, dilute acids and bases, and organic solvents
- At high temperatures, carbon becomes highly reactive and combines directly with many elements, including oxygen
- Carbon at high temperatures also reduces water, metal oxides, oxoanions (e.g., phosphate in phosphate rock), hydrogen

Oxides of Carbon

- Carbon forms CO and CO2.
- CO is very toxic (binds irreversibly to Fe in hemoglobin, causing respiratory arrest).
- CO also has a lone pair on C, which is unusual.
- CO is a good Lewis base Ni(CO)4 forms when Ni is warmed in CO
- CO can be used as a fuel 2CO(g) + O2(g) → 2CO2(g) ΔH = -566 kJ Chapter 22 22-13
- CO is a good reducing agent Fe3O4(s) + 4CO(g) → 3Fe(s) + 4CO2(g)
- CO2 is produced when organic compounds are burned in oxygen: C(s) + O2(g) → CO2(g) CH4(g) + 2O2(g) → CO2(g) + 2H2O(l)
- CO2 is produced by treating carbonates with acid.
- Fermentation of sugar to produce alcohol also produces CO2: C6H12O6(aq) → 2C2H5OH(aq) + 2CO2(g)
- At atmospheric pressure, CO2 condenses to form CO2(s) or dry ice.
- CO2 is used as dry ice (refrigeration), carbonation of beverages, washing soda (Na2CO3.10H2O) and baking soda (NaHCO3.10H2O).

Carbonic Acid and Carbonates

- When CO2 dissolves in water (moderately soluble) carbonic acid forms:

$$CO2(aq) + H2O(l)!H2CO3(aq)$$

- Carbonic acid is responsible for giving carbonated beverages a sharp acidic taste.
- Partial neutralization of H2CO3 gives hydrogen carbonates (bicarbonates) and full neutralization gives carbonates.
- Many minerals contain CO3 2-.
- At elevated temperatures CaCO3 decomposes:

$$CaCO3(s) \rightarrow CaO(s) + 2CO2(g)$$

- This reaction is the commercial source of lime, CaO.
- CaO reacts with water and CO2 to form CaCO3 which binds the sand in mortar: CaO(s) + H2O(l) ! Ca2+(aq) + 2OH- (aq)

Ca2+(aq) + 2OH- (aq) + CO2(aq) → CaCO3(s) + H2O(l)

Carbides

- Carbon combines with elements with a lower electronegativity to form carbides, which exist in three classes
- Salt-like carbides form with the most electropositive metals and are ionic, so they are hydrolyzed by water or dilute acid to give hydrocarbons
- Interstitial carbides are formed with transition metals, are very hard and have very high melting points, high metallic conductivity, and metallic luster; they consist of a metal with carbon atoms located in some of the interstitial sites (or holes) in the metal structure
- Covalent carbides include those of silicon and boron, which are close in size and electronegativity to carbon; they are completely covalent and form infinite network structures, are exceptionally hard materials widely used as abrasives 22.10 The Other Group 4A Elements: Si, Ge, Sn, and Pb General Characteristics of Group 4A Elements
- The electronegativities are low.
- The dominant oxidation state for Ge, Sn and Pb is +2.
- Carbon has a coordination number of 4, the other members have higher coordination numbers.
- C-C bonds are very strong, so C tends to form long chains.
- Because the Si-O bond is stronger than the Si-Si bond, Si tends to form oxides (silicates).

Exercise $22.S.1$

Compare the following properties on going down Group 4A:

- Metallic character
- Ionization energies
- Melting points
- Acid/base nature of oxides

22.10: The Other Group 14 Elements: Si, Ge, Sn, and Pb

- Si is nonmetallic/metalloid with only some of its chemistry similar to carbon
- Ge is a metalloid
- Sn and Pb are metallic
- Ionization energies and melting points decrease down the group, reflecting the change from nonmetal to metal
- Carbon bonds readily to itself
- This tendency diminishes on going down the group because the bond strength decreases considerably as the elements get larger
- Oxidation number +4 dominates near the top of the group, +2 becomes more stable down the group

Silicon

- Silicon exists in the earth's crust as silicon dioxide and over 800 silicate minerals
- Elemental silicon obtained by reduction of SiO2 with C or CaC2 at high temperature, purified by zone refining

$$SiO2(l) + 2C(s) \rightarrow Si(l) + 2CO(g)$$

- Silicon:
  - brittle gray-black metallic-looking solid
  - quite hard
  - high melting point
  - diamond-like tetrahedral network structure
  - inert at room temperature but reactive at high temperatures
- Used in semiconductor devices
- Silicon hydrides or silanes arise from reaction of Mg2Si with acids, giving a mixture of SiH4, Si2H6, Si3H8, Si4H10, Si5H12, and Si6H14

Exercise 22.S.1

What is the structure and bonding for Si_2H_6?

Silicon

- Silanes are quite reactive:
- The first two are stable. Chapter 22 22-15
- The others decompose to give SiH4, Si2H6, and H2.
- Much more reactive than the corresponding alkanes because of the availability of empty 3d orbitals that can be used to form bonds with another reactant
- They are spontaneously flammable in air. Group Work

Exercise 22.S.1

- SiO2, found as quartz, is quite hard. What feature of its structure gives rise to this hardness?

Silicon

- SiO2 exists as polymeric (SiO2)n, which has silicon covalently bonded to four bridging oxygen atoms.
- Extended covalent bonding network
- Hard, high-melting solid
- Glass is formed by heating together silicon dioxide, alkali metal and alkaline earth metal oxides, and sometimes other oxides, the particular mixture controlling the properties of the glass.
- Silicate structure is somewhat random in contrast to crystalline silicates
- Some bonds are under more strain than others, so the glass melts over a range of temperatures and can be softened without melting
- 90 % of the earthís crust is composed of compounds of Si and O.
- Silicates are compounds where Si has four O atoms surrounding it in a tetrahedral arrangement.
- The oxidation state of Si is +4.
- The silicate tetrahedra are building blocks for more complicated structures.
- Many silicates naturally with the basic structural unit being the SiO4 tetrahedron occurring in several varieties:
  - singly
  - small groups sharing oxygen atoms
  - small cyclic groups
  - infinite chains
  - double-stranded chains (or bands)
  - infinite sheets
- These few structures form many hundreds of minerals by combination of silicate anions with metal cations.

Silicon

- The silicate structure is reflected in the physical structure of minerals such as mica and asbestos.

22.11: Boron

- Black crystalline element, extremely hard and brittle, low density, high melting point and boiling point, low electrical conductivity (so classified as a semiconductor), used in semiconductor electronics and added to steel to increase strength and to copper to increase electrical conductivity
- Similarities of some properties to those of carbon, of others to those of silicon (due to Chapter 22 22-16 the diagonal relationship leading to similar size and electronegativity)
- Carbon, silicon, and boron all form covalently-bonded extended network solids and covalent halides

- Occurs in deposits of borax, Na2B4O7 . 10H2O
- Borax used as an additive to laundry detergents to soften the water.
- Which U.S. president was associated with Twenty Mule Team Borax?
- Resembles metals in its physical properties but is more like nonmetals chemically
- Chemical behavior is complex and unusual: ionization energy is unusually high, so formation of a cation is difficult, high electronegativity (comparable to nonmetals)
- All its compounds are covalent

Exercise $22.S.1$

- What is the valence electron configuration of boron? How many covalent bonds will it normally form?

Boron

- Valence electron configuration 2s2 2p1 , so forms only three normal covalent bonds, but electron deficiency makes it a good Lewis acid
- Oxidation number +3 common, but others found in boranes
- B3+ does not exist in aqueous solution. Why not?
- Reacts with F2 and Cl2 to give trihalides
- Great affinity for O2, which is used to remove oxygen from metal oxides to purify molten metals
- B reacts with N2 at high temperature to give solid BN.
- BN is very stable due to its graphite-like structure, which arises from the presence of only 3 valence electrons and the tendency to use sp2 hybrid orbitals.
- BN is also known in a diamond-like structure, which is formed by application of high temperature and pressure, and is extremely hard and is used as an abrasive.
- Large number of hydrides have been prepared
- BH3 is known but very unstable (reactive)
- Simplest stable one is diborane, B2H6, which decomposes to other boranes, e.g. B5H9, when heated
- Unusual structure and bonding in the boranes, in which hydrogens act as bridges between boron and the B-H-B arrangement shares two electrons between three atoms (called three center bonding)
- Because of their electron deficiencies, boranes are highly reactive
- Diborane is very reactive:

$$B2H6(g) + 3O2(g) \rightarrow B2O3(s) + 3H2O(g)$$

with ΔH = -2030 kJ

- Some boranes are reactive (B5H9) while some are stable in air at room temperature (B10H14).
- B2O3 is the only important boron oxide.
- Boric acid, H3BO3 or B(OH)3 is a weak acid (Ka = 5.8 × 10-10).
- Boric acid is used as an eye wash.

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23: CHEMISTRY OF COORDINATION CHEMISTRY

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. These include the *d*-block (groups 3–11) and f-block element elements. The variety of properties exhibited by transition metals is due to their complex valence shells. Unlike most main group metals where one oxidation state is normally observed, the valence shell structure of transition metals means that they usually occur in several different stable oxidation states. In addition, electron transitions in these elements can correspond with absorption of photons in the visible electromagnetic spectrum, leading to colored compounds. Because of these behaviors, transition metals exhibit a rich and fascinating chemistry.

23.1: Metal Complexes

23.2: Ligands with more than one Donor Atom

23.3: Nomenclature of Coordination Chemistry

23.4: Isomerization

23.5: Color and Magnetism

23.6: Crystal Field Theory

23.E: Chemistry of Coordination Chemistry (Exercises)

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23.1: Metal Complexes

Learning Objectives

- To introduce complex ions and the basic principles of metal-ligand bonding

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (in some cases, the bonding is actually more complicated than that. The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.

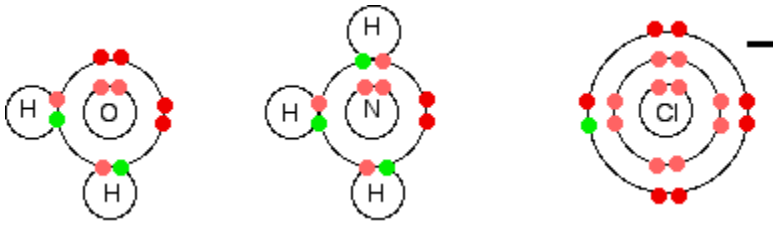


Figure 23.1.1: Simple Bohr diagram bonding in water, ammonia, and the chloride ion.

What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion. All ligands are lone pair donors. In other words, all ligands function as Lewis bases.

Bonding in Simple Complex Ions

We are going to look in detail at the bonding in the complex ion formed when water molecules attach themselves to an aluminum ion to give $Al(H_2O)_6^{3+}$. Start by thinking about the structure of a naked aluminum ion before the water molecules bond to it.

Example 23.1.1: $Al(H_2O)_6^{3+}$

Aluminum has the electronic structure

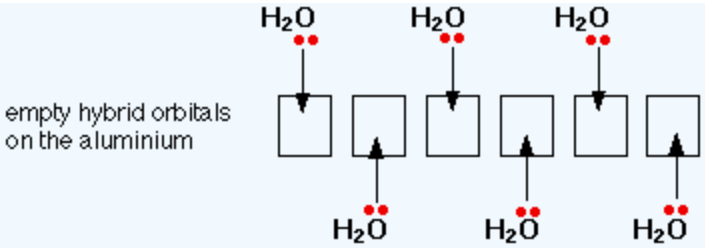
$$1s^2 2s^2 2p^6 3s^2 3p_x^1$$

When it forms an Al^{3+} ion it loses the 3-level electrons to leave

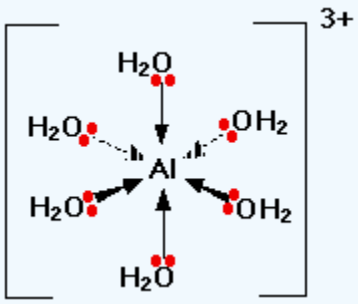
$$1s^2 2s^2 2p^6$$

That means that all the 3-level orbitals are now empty. The aluminium uses all six of these empty 3-level orbitals to accept lone pairs from six water molecules. It re-organizes (hybridizes) the 3s, the three 3p, and two of the 3d orbitals to produce six new orbitals all with the same energy.

You might wonder why it chooses to use six orbitals rather than four or eight or whatever. Six is the maximum number of water molecules that will fit around an aluminum ion (and most other metal ions) due to steric constraints. By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.



Only one lone pair is shown on each water molecule. The other lone pair is pointing away from the aluminum and so isn't involved in the bonding. The resulting ion looks like this:



Because of the movement of electrons towards the center of the ion, the 3+ charge is no longer located entirely on the aluminum, but is now spread over the whole of the ion. Because the aluminum is forming 6 bonds, the co-ordination number of the aluminum is said to be 6. The co-ordination number of a complex ion counts the number of co-ordinate bonds being formed by the metal ion at its center.

In a simple case like this, that obviously also counts the number of ligands - but that is not necessarily so, as you will see later. Some ligands can form more than one co-ordinate bond with the metal ion.

Example 23.1.2: $Fe(H_2O)_6^{3+}$

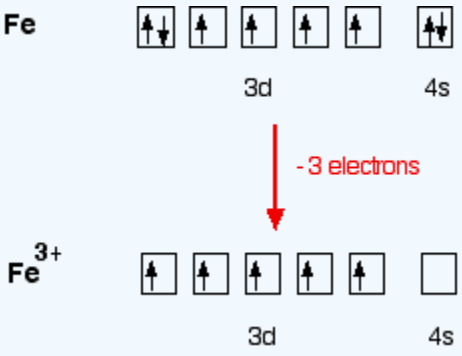
Iron has the electronic structure

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$$

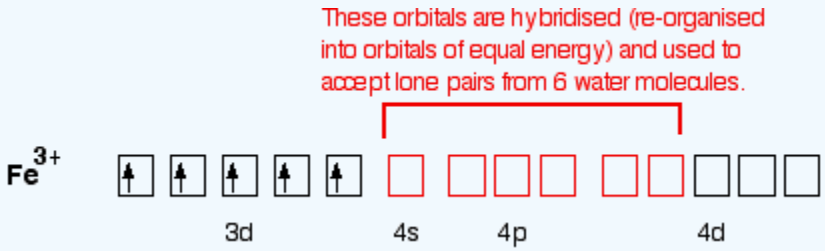
When it forms an Fe^{3+} ion it loses the 4s electrons and one of the 3d electrons to leave

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$$

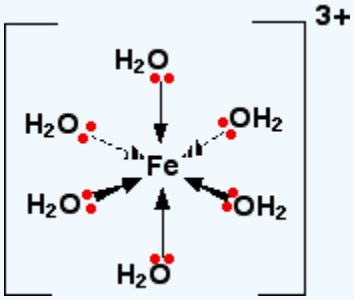
Looking at this as electrons-in-boxes, at the bonding level:



The single electrons in the 3d level are NOT involved in the bonding in any way. Instead, the ion uses 6 orbitals from the 4s, 4p and 4d levels to accept lone pairs from the water molecules. Before they are used, the orbitals are re-organized (hybridized) to produce 6 orbitals of equal energy.



Once the co-ordinate bonds have been formed, the ion looks exactly the same as the equivalent aluminium ion.



Because the iron is forming 6 bonds, the co-ordination number of the iron is 6.

Example 23.1.3: $CuCl_4^{2-}$

This is a simple example of the formation of a complex ion with a negative charge.

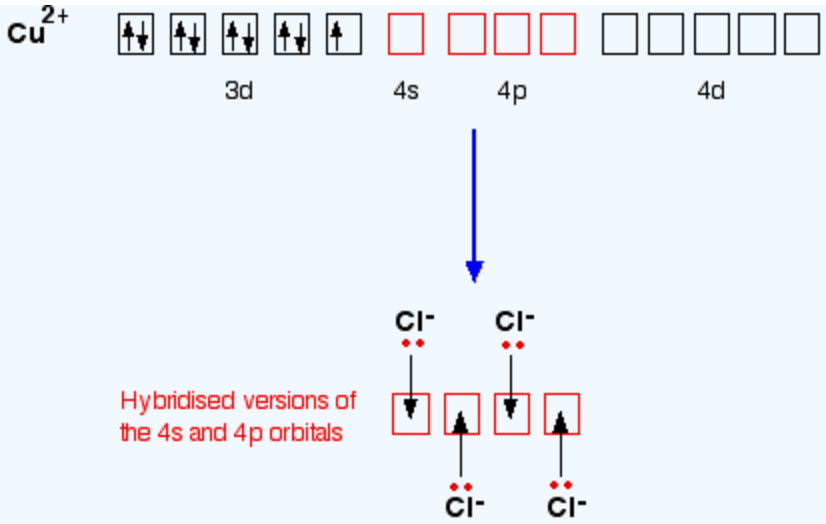
Copper has the electronic structure

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$$

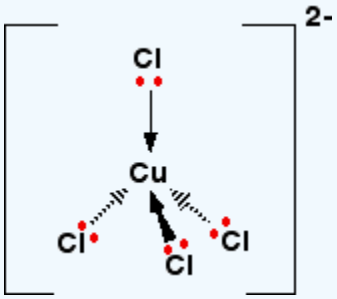
When it forms a Cu^{2+} ion it loses the 4s electron and one of the 3d electrons to leave

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$$

To bond the four chloride ions as ligands, the empty 4s and 4p orbitals are used (in a hybridized form) to accept a lone pair of electrons from each chloride ion. Because chloride ions are bigger than water molecules, you can't fit 6 of them around the central ion - that's why you only use 4.



Only one of the 4 lone pairs on each chloride ion is shown. The other three are pointing away from the copper ion, and aren't involved in the bonding. That gives you the complex ion:



The ion carries 2 negative charges overall. That comes from a combination of the 2 positive charges on the copper ion and the 4 negative charges from the 4 chloride ions. In this case, the co-ordination number of the copper is 4.

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23.2: Ligands with more than one Donor Atom

Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced. Monodentate ligands bind through only one donor atom. Monodentate means "one-toothed." The halides, phosphines, ammonia and amines seen previously are monodentate ligands. Bidentate ligands bind through two donor sites. Bidentate means "two-toothed." An example of a bidentate ligand is ethylenediamine. It can bind to a metal via two donor atoms at once.



Figure 23.2.1: The hypothetical "lobster ligand" binds to the Ni^{2+} via two donor sites.

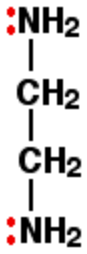
Bidentate binding allows a ligand to bind more tightly. Tridentate ligands, which bind through three donors, can bind even more tightly, and so on. This phenomenon is generally called the "**chelate effect**." This term comes from the Greek chelos, meaning "crab." A crab does not have any teeth at all, but it does have two claws for tightly holding onto something for a couple of reasons. A very simple analogy is that, if you are holding something with two hands rather than one, you are not as likely to drop it.

Complex metal ions containing more complicated ligands

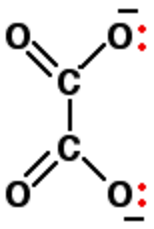
In the examples previously disccussed, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone pairs are pointing in the wrong direction. Some ligands, however, have rather more teeth! These are known generally as multidentate or polydentate ligands, but can be broken down into a number of different types.

Bidentate ligands

Bidentate ligands have two lone pairs, both of which can bond to the central metal ion. The two commonly used examples are 1,2-diaminoethane (old name: ethylenediamine - often given the abbreviation "en"), and the ethanedioate ion (old name: oxalate).

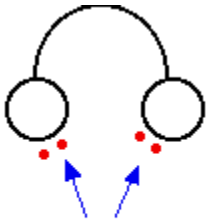


1,2-diaminoethane



ethanedioate ion

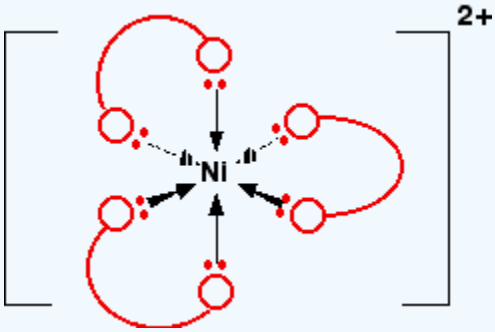
In the ethanedioate ion, there are lots more lone pairs than the two shown, but these are the only ones we are interested in. You can think of these bidentate ligands rather as if they were a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snuggly around a metal ion.



These can both be used to form co-ordinate bonds with the same metal ion.

Example 23.2.1: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

You might find this abbreviated to $[Ni(en)_3]^{2+}$. The structure of the ion looks like this:



In this case, the "ear pieces" are the nitrogen atoms of the NH2 groups - and the "bit that goes over your head " is the $-CH_2CH_2-$ group. If you were going to draw this in an exam, you would obviously want to draw it properly - but for learning purposes, drawing all the atoms makes the diagram look unduly complicated!

Notice that the arrangement of the bonds around the central metal ion is exactly the same as it was with the ions with 6 water molecules attached. The only difference is that this time each ligand uses up two of the positions - at right angles to each other.

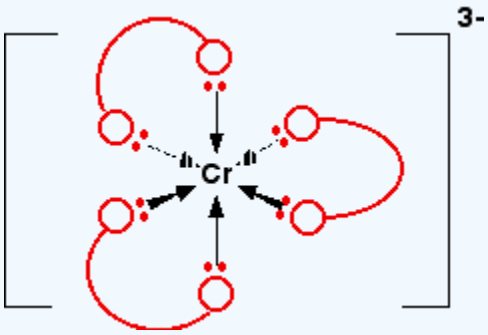
Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the number of bonds, not the number of ligands.

Example 5: $Cr(C_2O_4)_3^{3-}$

This is the complex ion formed by attaching 3 ethanedioate (oxalate) ions to a chromium(III) ion. The shape is exactly the same as the previous nickel complex. The only real difference is the number of charges. The original chromium ion carried 3+ charges, and each ethanedioate ion carried -2, i.e.,

$$(+3) + (3 \times -2) = -3.$$

The structure of the ion looks like this:

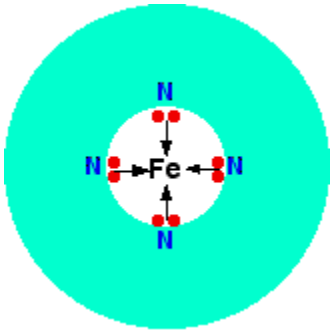


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

A Quadridentate Ligand

A quadridentate ligand has four lone pairs, all of which can bond to the central metal ion. An example of this occurs in haemoglobin (American: hemoglobin). The functional part of this is an iron(II) ion surrounded by a complicated molecule called heme. This is a sort of hollow ring of carbon and hydrogen atoms, at the center of which are 4 nitrogen atoms with lone pairs on them. Heme is one of a group of similar compounds called porphyrins. They all have the same sort of ring system, but with different groups attached to the outside of the ring. You aren't going to need to know the exact structure of the haem at this level.

We could simplify the heme with the trapped iron ion as:



Each of the lone pairs on the nitrogen can form a co-ordinate bond with the iron(II) ion - holding it at the center of the complicated ring of atoms. The iron forms 4 co-ordinate bonds with the heme, but still has space to form two more - one above and one below the plane of the ring. The protein globin attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids. The interesting bit is the other position.

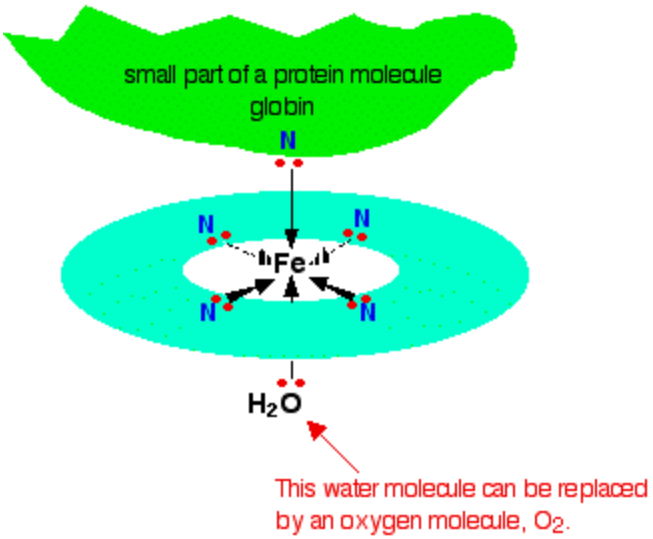


Figure 23.2.2: Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds.

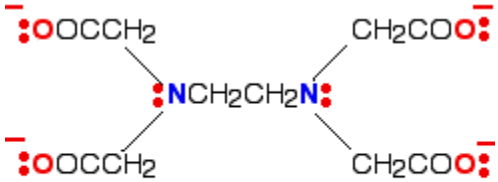
The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O_2) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin which returns to the lungs to get some more.

Carbon Monoxide Poisoning

You probably know that carbon monoxide is poisonous because it reacts with hemeoglobin. It bonds to the same site that would otherwise be used by the oxygen - but it forms a very stable complex. The carbon monoxide doesn't break away again, and that makes that hemeoglobin molecule useless for any further oxygen transfer.

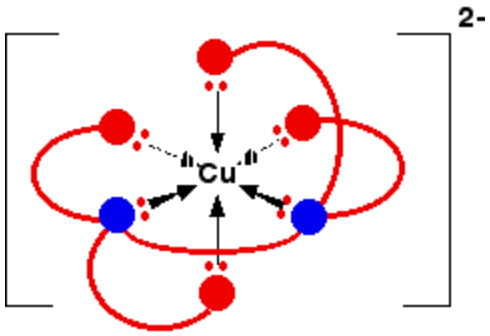
A Hexadentate Ligand

A hexadentate ligand has 6 lone pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA. The diagram shows the structure of the ion with the important atoms and lone pairs picked out.



the EDTA^{4-} ion

The EDTA ion entirely wraps up a metal ion using all 6 of the positions that we have seen before. The co-ordination number is again 6 because of the 6 co-ordinate bonds being formed by the central metal ion. The diagram below shows this happening with a copper(II) ion. Here is a simplified version. Make sure that you can see how this relates to the full structure above.



the [Cu(EDTA)]$^{2-}$ ion

The overall charge, of course, comes from the 2+ on the original copper(II) ion and the 4- on the $EDTA^{4-}$ ion.

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23.3: Nomenclature of Coordination Chemistry

Learning Objectives

- To learn the basis for complex ion and compound nomenclature

Coordination complexes have their own classes of isomers, different magnetic properties and colors, and various applications (photography, cancer treatment, etc), so it makes sense that they would have a naming system as well. Consisting of a metal and ligands, their formulas follow the pattern [Metal ligands]$^{\pm Charge}$, while names are written Prefix Ligands Metal (Oxidation State).

Introduction

According to the Lewis Acid-Base theory, ligands are Lewis bases since they can donate electrons to the central metal atom. The metals, in turn, are Lewis acids since they accept electrons. **Coordination complexes** consist of a ligand and a metal center cation and their charge can be positive, negative, or neutral. **Coordination compounds** are neutral compounds that contain at least one complex ions. Example of coordination complexes and compounds are:

- Complex Cation: $[Co(NH_3)_6]^{3+}$
- Complex Anion: $[CoCl_4(NH_3)_2]^-$
- Neutral Complex: $[CoCl_3(NH_3)_3]$
- Coordination Compound: $K_4[Fe(CN)_6]$

A ligand can be an anion or a neutral molecule that *donates an electron pair* to the complex (NH_3, H_2O, Cl^-). The number of ligands that attach to a metal depends on whether the ligand is **monodentate** or **polydentate**.

Rules to Complex Ion Nomenclature

To begin naming coordination complexes, here are some things to keep in mind.

1. Ligands are named first in alphabetical order.
2. The name of the metal comes next.
3. The oxidation state of the metal follows, noted by a Roman numeral in parentheses (II, IV).

Rule 1: Anionic Ligands

Ligands that act as anions which end in "-ide" are replaced with an ending "-o" (e.g., Chloride → Chloro). Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively (e.g., Nitrite → Nitrito, Nitrate → Nitrato).

Table 23.3.1: Anionic Monodentate Ligands

Molecular Formula	Ligand Name	Molecular Formula	Ligand Name
F^-	Fluoro	OH^-	Hydroxo
Cl^-	Chloro	SO_4^{2-}	Sulfato
Br^-	Bromo	$S_2O_3^{2-}$	Thiosulfato
I^-	Iodo	NO_2^-	Nitrito-N-; Nitro
O^{2-}	Oxo	ONO^-	Nitrito-O-; Nitrito
CN^-	Cyano	SCN^-	Thiocyanato-S-; Thiocyanato

Molecular Formula	Ligand Name	Molecular Formula	Ligand Name
NC^-	Isocyano	NCS^-	Thiocyanato-N-; Isothiocyanato

Rule 2: Neutral Ligands

Most neutral molecules that are ligands carry their normal name. The few exceptions are the first four on the chart: ammine, aqua, carbonyl, and nitrosyl.

Table 23.3.2: Select Neutral Monodentate Ligands. Note: Ammine is spelled with two m's when referring to a ligand. Amines are a class of organic nitrogen-containing compounds.

Molecular Formula of Ligand	Ligand Name
NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
NO	Nitrosyl
CH_3NH_2	Methylamine
C_5H_5N	Pyridine

Polydentate ligands follow the same rules for anions and neutral molecules.

Table 23.3.3: Select Polydentate ligands

Short name	Extended name
en	Ethylenediamine
ox^{2-}	Oxalato
$EDTA^{4-}$	Ethylenediaminetetraacetato

Rule 3: Ligand Multiplicity

The number of ligands present in the complex is indicated with the prefixes di, tri, etc. The exceptions are polydentates that have a prefix already in their name (en and $EDTA^{4-}$ are the most common). When indicating how many of these are present in a coordination complex, put the ligand's name in parentheses and use *bis* (for two ligands), *tris* (for three ligands), and *tetrakis* (for four ligands).

Table 23.3.4: Prefixes for indicating number of ligands in a complex.

Number of Ligands	Monodentate Ligands	Polydentate Ligands
1	mono	-
2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis

Prefixes always go before the ligand name; they are not taken into account when putting ligands in alphabetical order. Note that "mono" often is not used. For example, $[FeCl(CO)_2(NH_3)_3]^{2+}$ would be called triamminedicarbonylchloroiron(III) ion. Remember that ligands are always named first, before the metal is.

Example 23.3.1

What is the name of this complex ion: $[CrCl_2(H_2O)_4]^+$?

Solution

Let's start by identifying the ligands. The ligands here are Cl and H_2O. Therefore, we will use the monodentate ligand names of "chloro" and "aqua". Alphabetically, aqua comes before chloro, so this will be their order in the complex's name. There are 4 aqua's and 2 chloro's, so we will add the number prefixes before the names. Since both are monodentate ligands, we will say "tetra[aqua]di[chloro]".

Now that the ligands are named, we will name the metal itself. The metal is Cr, which is chromium. Therefore, this coordination complex is called tetraaquadichlorochromium(III) ion. See the next section for an explanation of the (III).

Exercise 23.3.1

What is the name of this complex ion: $[CoCl_2(en)_2]^+$?

Answer available at the end of this section.

Rule 4: The Metals

When naming the metal center, you must know the formal metal name and the oxidation state. To show the oxidation state, we use Roman numerals inside parenthesis. For example, in the problems above, chromium and cobalt have the oxidation state of +3, so that is why they have (III) after them. Copper, with an oxidation state of +2, is denoted as copper(II). If the overall coordination complex is an anion, the ending "-ate" is attached to the metal center. Some metals also change to their Latin names in this situation. Copper +2 will change into cuprate(II). The following change to their Latin names when part of an anion complex:

Table 23.3.5: Latin terms for Select Metal Ion

Transition Metal	Latin
Iron	Ferrate
Copper	Cuprate
Tin	Stannate
Silver	Argentate
Lead	Plumbate
Gold	Aurate

The rest of the metals simply have -ate added to the end (cobaltate, nickelate, zincate, osmate, cadmate, platinate, mercurate, etc. Note that the -ate tends to replace -um or -ium, if present).

Finally, when a complex has an overall charge, "ion" is written after it. This is not necessary if it is neutral or part of a coordination compound (Example 23.3.3). Here are some examples with determining oxidation states, naming a metal in an anion complex, and naming coordination compounds.

Example 23.3.2

What is the name of $[Cr(OH)_4]^-$?

Solution

Immediately we know that this complex is an anion. There is only one monodentate ligand, hydroxide. There are four of them, so we will use the name "tetrahydroxo". The metal is chromium, but since the complex is an anion, we will have to use the "-ate" ending, yielding "chromate". The oxidation state of the metal is 3 (x+(-1)4=-1). Write this with Roman numerals and parentheses (III) and place it after the metal to get tetrahydroxochromate(III) ion.

Exercise 23.3.2

What is the name of $[CuCl_4]^{2-}$?

Answer available at the end of this section.

A last little side note: when naming a coordination compound, it is important that you name the cation first, then the anion. You base this on the charge of the ligand. Foe xample, for $NaCl$. The the positive Na cation comes first and the negative Cl^- anion follows.

Example 23.3.3

What is the name of $[Pt(NH_3)_4][Pt(Cl)_4]$?

Solution

NH_3 is neutral, making the first complex positively charged overall. Cl has a -1 charge, making the second complex the anion. Therefore, you will write the complex with NH_3 first, followed by the one with Cl (the same order as the formula). This coordination compound is called tetraammineplatinum(II) tetrachloroplatinate(II).

Exercise 23.3.3: The Nitro/Nitrito Ambidentate Ligand

What is the name of $[CoCl(NO_2)(NH_3)_4]^+$?

Answer available at the end of this section.

Writing Formulas of Coordination Complexes

While chemistry typically follow the nomenclature rules for naming complexes and compounds, there is disagreement with the rules for constructing formulas of inorganic complexes. For example, the order of ligand names in their formula has been ambiguous with different conventions being used (charged vs neutral, number of each ligand, etc.). In 2005, IUPAC adopted the recommendation that all ligand names in formulas be listed **alphabetically** (in the same way as in the naming convention) irrespective of the charge or number of each ligand type.

However, this rule is not adhered to in many chemistry laboratories. For practice, the order of the ligands in chemical formulas does not matter as long as you write the transition metal first, which is the stance taken here.

Examples 23.3.4

Write the chemical formulas for:

a. Amminetetraaquachromium(II) ion
b. Amminesulfatochromium(II)

Solution

a. Amminetetraaquachromium(II) ion could be written as $[Cr(H_2O)_4(NH_3)]^{+2}$ or $[Cr(NH_3)(H_2O)_4]^{+2}$.
b. Amminesulfatochromium (II) could be written as $[Cr(SO_4)(NH_3)]$ or $[Cr(NH_3)(SO_4)]$.

Exercise 23.3.4

Write the chemical formulas for

a. Amminetetraaquachromium (II) sulfate
b. Potassium hexacyanoferrate (III)

Answer available at the end of this section.

Answers

Exercise 23.3.1

We take the same approach. There are two chloro and ethylenediamine ligands. The metal is Co, cobalt. We follow the same steps, except that en is a polydentate ligand with a prefix in its name (ethylene**di**amine), so "bis" is used instead of "di", and parentheses are added. Therefore, this coordination complex is called dichlorobis(ethylenediamine)cobalt(III) ion.

Exercise 23.3.2

tetrachlorocuprate(II) ion

Exercise 23.3.3**: The Nitro/Nitrito Ambidentate Ligand**

This coordination complex is called tetraamminechloronitrito-N-cobalt(III). N comes before the O in the symbol for the nitrite ligand, so it is called nitrito-N. If an O came first, as in $[CoCl(ONO)(NH_3)_4]^+$, the ligand would be called nitrito-O, yielding the name tetraamminechloronitrito-O-cobalt(III).

Nitro (for NO_2) and nitrito (for ONO) can also be used to describe the nitrite ligand, yielding the names tetraamminechloronitrocobalt(III) and tetraamminechloronitritocobalt(III).

Exercise 23.3.4

a. Amminetetraaquachromium (II) sulfate can be written as $[Cr(H_2O)_4(NH_3)]SO_4$. Although $[Cr(NH_3)(H_2O)_4]SO_4$ is also acceptable.
b. Potassium hexacyanoferrate (III) is be written as $K_3[Fe(CN)_6]$

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23.4: Isomerization

Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $(NH_3)_2PtCl_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

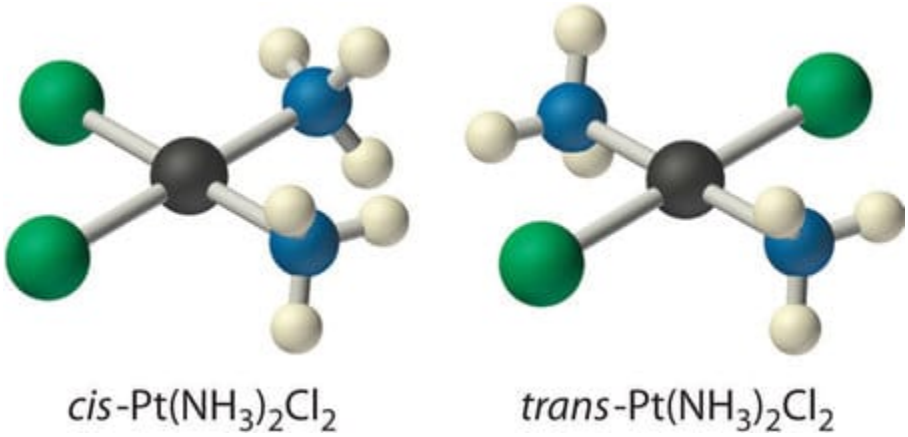


Figure 23.4.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of coordination compounds bond together is discussed in the chapter of Lewis acids and bases. For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by MIT chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two ammines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced, and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

Exercise 23.4.1

Draw the cis and trans isomers of the following compounds:

a. $(NH_3)_2IrCl(CO)$
b. $(H_3P)_2PtHBr$
c. $(AsH_3)_2PtH(CO)$

Exercise 23.4.2

Only one isomer of (tmeda)$PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

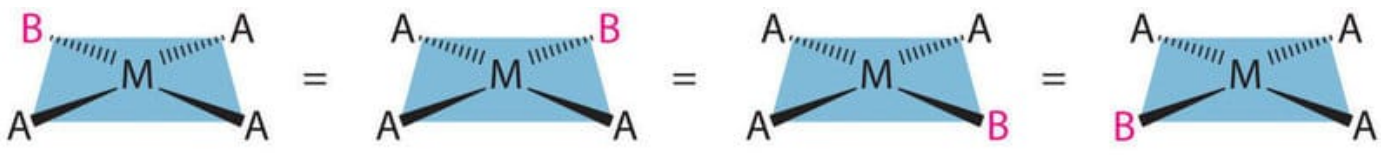
Geometric Isomers

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

Planar Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



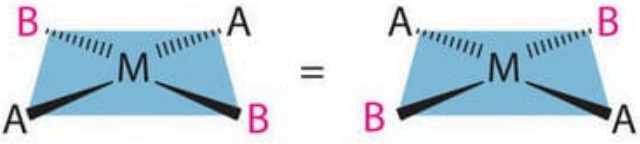
MA_3B square planar complex

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (cis), in which case

the B ligands must also be cis, or the A ligands can be across from one another (trans), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:



MA_2B_2 square planar complex, *cis* isomer

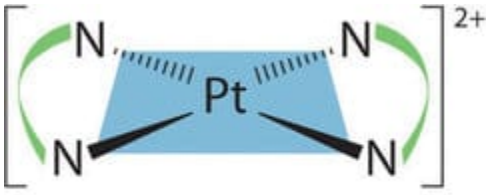


MA_2B_2 square planar complex, *trans* isomer

Figure 23.4.1).

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

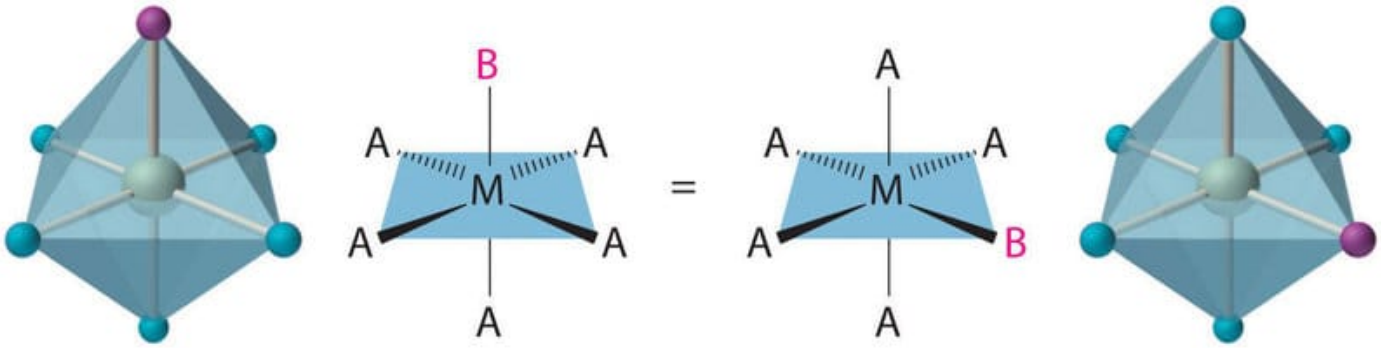
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



$[Pt(en)_2]^{2+}$

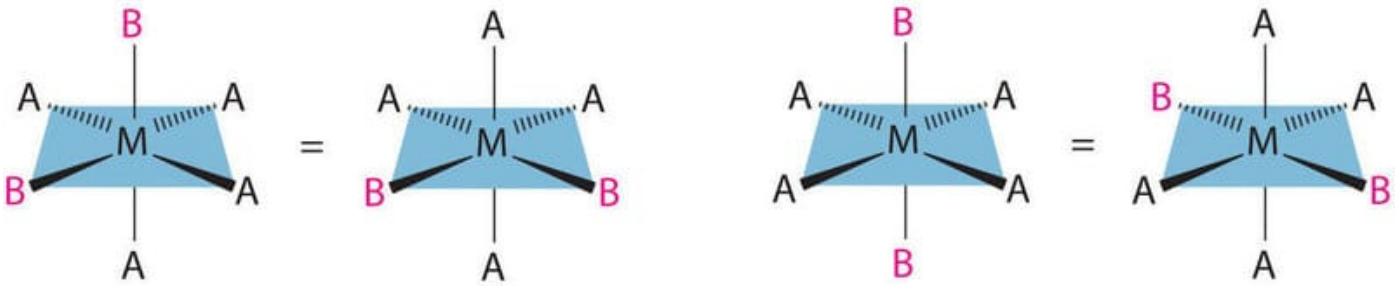
Octahedral Isomers

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:



MA_5B octahedral complex

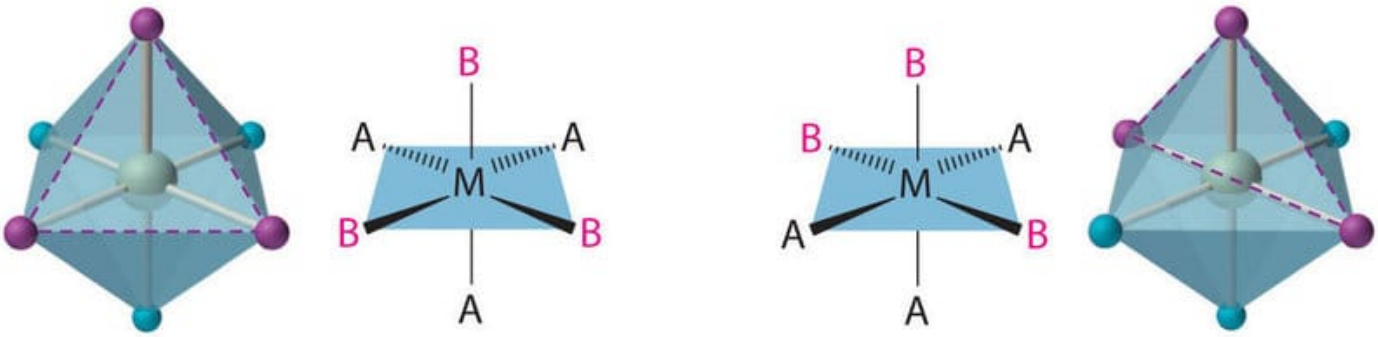
If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:



MA_4B_2 octahedral complex, *cis* isomer

MA_4B_2 octahedral complex, *trans* isomer

Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



MA_3B_3 octahedral complex, *fac* isomer

MA_3B_3 octahedral complex, *mer* isomer

Example 23.4.1

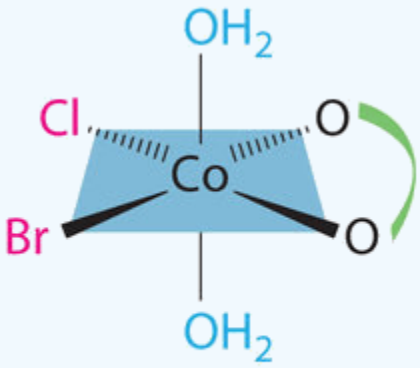
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Given: formula of complex

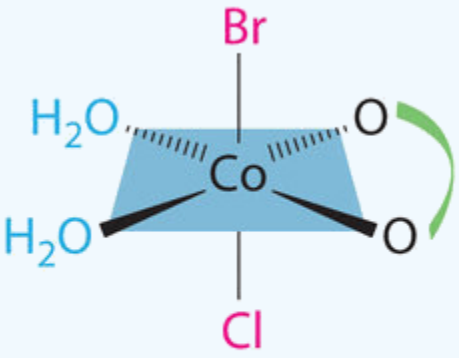
Asked for: structures of geometrical isomers

Solution

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:

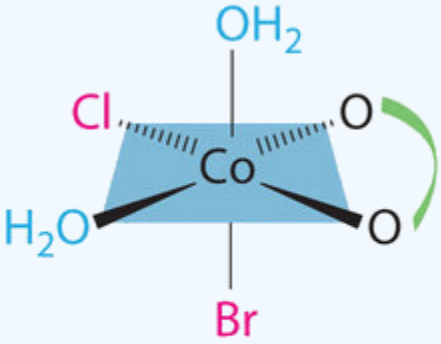


H_2O's *trans*

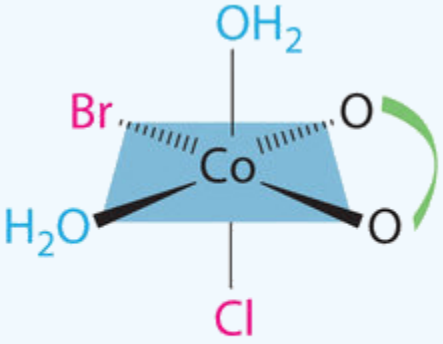


Br, Cl *trans*

In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:



H_2O's *cis*; Br, Cl *cis*; Cl *trans* to O



H_2O's *cis*; Br, Cl *cis*; Br *trans* to O

This complex can therefore exist as four different geometrical isomers.

Exercise 23.4.1

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer available at the end of this section.

Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

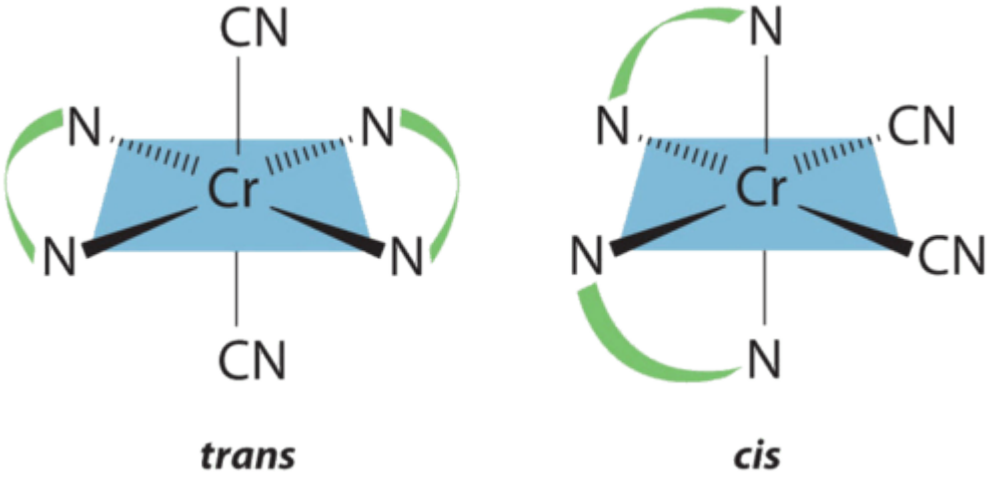
Contributors and Attributions

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Answers

Exercise 23.4.1

Two geometrical isomers are possible: trans and cis.



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23.5: Color and Magnetism

Learning Objectives

- To get a simple overview of the origin of color and magnetism in complex ions.

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum and have certain characteristics, including amplitude, wavelength, and frequency (Figure 23.5.1).

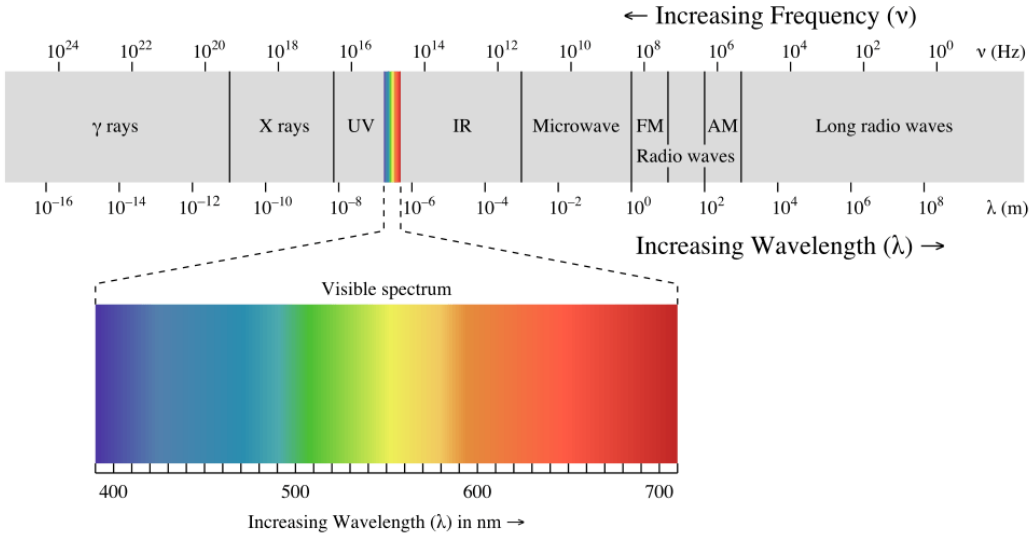


Figure 23.5.1: Electromagnetic spectrum with light highlighted. (CC -SA-BY 2.0 unported; Philip Ronan).

General properties of all electromagnetic radiation include:

1. Electromagnetic radiation can travel through empty space, while most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through to be heard.
2. The speed of light (c) is always a constant (2.99792458 x 10^8 m s^{-1}).
3. Wavelengths (λ) are measured between the distances of either crests or troughs.

The energy of a photon is expressed by Planck's law in terms of the frequency (u) of the photon

$$E = hu \tag{23.5.1}$$

since $\lambda u = c$ for all light Plancks law can be also expressed in terms of the wavelength of the photon

$$E = hu = \frac{hc}{\lambda} \tag{23.5.2}$$

If white light is passed through a prism, it splits into all the colors of the rainbow (Figure 23.5.2). Visible light is simply a small part of an electromagnetic spectrum most of which we cannot see - gamma rays, X-rays, infra-red, radio waves and so on. Each of these has a particular wavelength, ranging from 10^{-16} meters for gamma rays to several hundred meters for radio waves. Visible light has wavelengths from about 400 to 750 nm (1 nanometer = 10^{-9} meters).

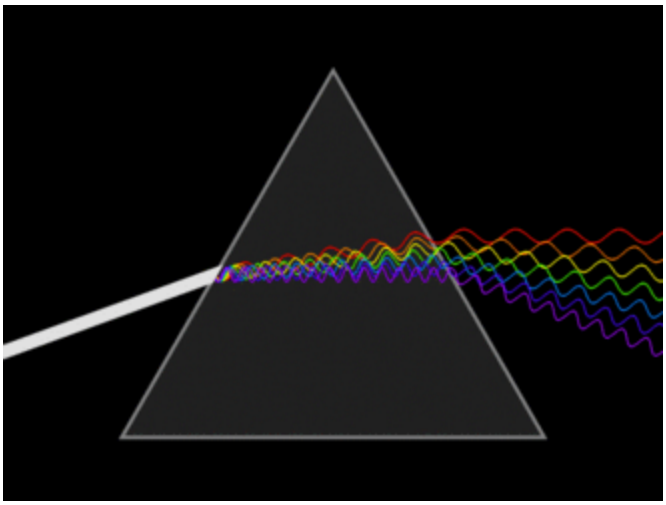
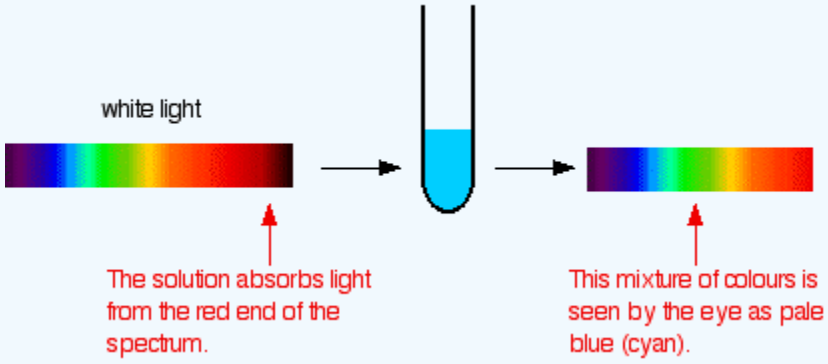


Figure 23.5.2: A triangular prism, dispersing light; waves shown to illustrate the differing wavelengths of light. (Public Domain; Lucas V. Barbosa).

Example 23.5.1: Blue Color of Copper (II) Sulfate in Solution

If white light (ordinary sunlight, for example) passes through copper(II) sulfate solution, some wavelengths in the light are absorbed by the solution. Copper(II) ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through copper(II) sulfate solution.



Working out what color you will see is not easy if you try to do it by imagining "mixing up" the remaining colors. You would not have thought that all the other colors apart from some red would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors.

Origin of Colors

The process of absorption involves the excitation of the valence electrons in the molecule typically from the low lying level called the Highest Occupied Molecular Orbital (HOMO) into a higher lying state called the the Lowest Unoccupied Molecular Orbital (**LUMO**). When this HOMO and LUMO transition (Figure 23.5.3) involves the absorption of visible light, the sample is colored.

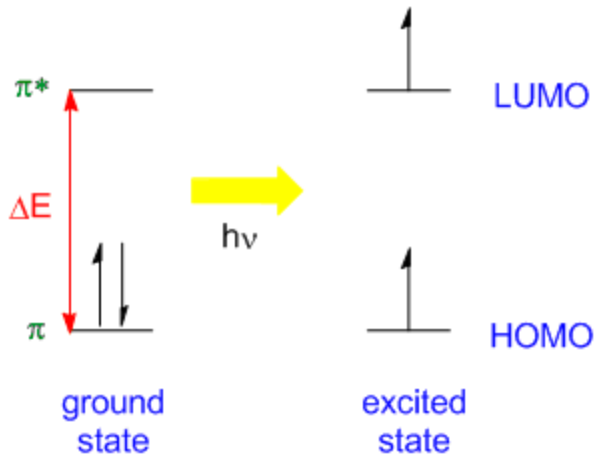


Figure 23.5.4: The general electron excitation process from a HOMO to a LUMO.

The HOMO-LUMO energy difference

$$\Delta E = E_{HOMO} - E_{LUMO} \tag{23.5.3}$$

depends on the nature of the molecule and can be connected to the wavelength of the light absorbed

$$\Delta E = hu = \frac{hc}{\lambda} \tag{23.5.4}$$

Equation 23.5.4 is the most important equation in the field of light-matter interactions (spectroscopy).

As Example 23.5.1 demonstrated, when white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other (Figure 23.5.5). Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

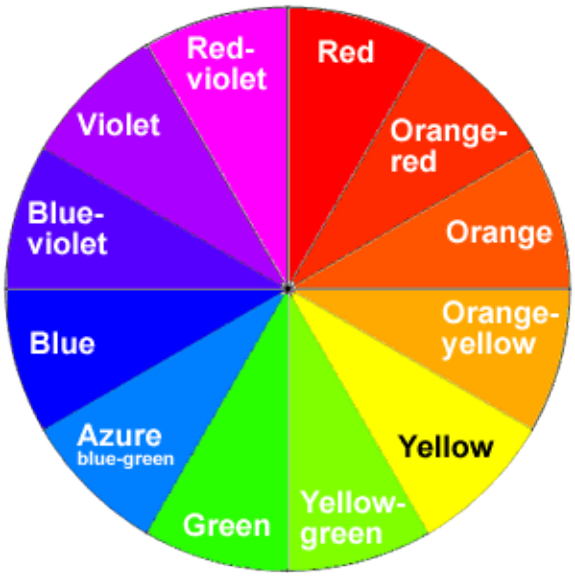


Figure 23.5.5: The color wheel used to identify the color of species.

Colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing

up all the other wavelengths of light is its complementary color. Copper(II) sulfate solution is pale blue (cyan) because it absorbs light in the red region of the spectrum and cyan is the complementary color of red (Table 23.5.1).

Table 23.5.1: The Visible Spectrum

Color	Wavelength (nm)	ΔE HOMO - LUMO gap (eV)
UV	100 - 400	12.4 - 3.10
Violet	400 - 425	3.10 - 2.92
Blue	425 - 492	2.92 - 2.52
Green	492 - 575	2.52 - 2.15
Yellow	575 - 585	2.15 - 2.12
Orange	585 - 647	2.12 - 1.92
Red	647 - 700	1.92 - 1.77
Near IR	700 - 10,000	1.77 - 0.12

If the compound absorbs in one region of the spectra, it appears with the opposite (complementary) color, since all of the absorbed color has been removed. For example:

- the material absorbs violet light ⇒ color is yellow
- the material absorbs blue light ⇒ color is orange
- the material absorbs yellow-green light ⇒ color is red-violet

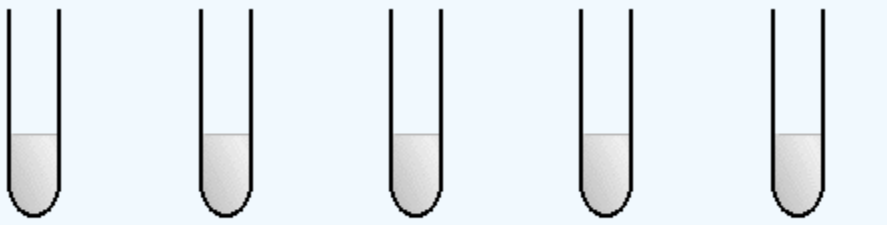
The Origin of Color in Complex Ions

We often casually talk about the transition metals as being those in the middle of the Periodic Table where d orbitals are being filled, but these should really be called d block elements rather than transition elements (or metals). The definition of a transition metal is one which forms one or more stable ions which have incompletely filled d orbitals. Zinc with the electronic structure [Ar] $3d^{10}4s^2$ does not count as a transition metal whichever definition you use. In the metal, it has a full 3d level. When it forms an ion, the 4s electrons are lost - again leaving a completely full 3d level. At the other end of the row, scandium ([Ar] $3d^14s^2$) does not really counts as a transition metal either. Although there is a partially filled d level in the metal, when it forms its ion, it loses all three outer electrons. The Sc^{3+} ion does not count as a transition metal ion because its 3d level is empty.

Example 23.5.3: Hexaaqua Metal Ions

The diagrams show the approximate colors of some typical hexaaqua metal ions, with the formula $[\ M(H_2O)_6\ ]^{n+}$. The charge on these ions is typically 2+ or 3+.

- Non-transition metal ions

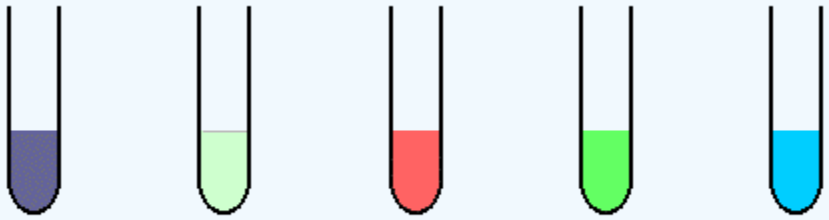


$[\ Mg(H_2O)_6\ ]^{2+}$ $[\ Al(H_2O)_6\ ]^{3+}$ $[\ Ca(H_2O)_6\ ]^{2+}$ $[\ Sc(H_2O)_6\ ]^{3+}$ $[\ Zn(H_2O)_6\ ]^{2+}$

These ions are all colorless.

Ions are [Mg(H2O)6] two plus, [Al(H2O)6] three plus, [Ca(H2O)6] two plus, [Sc(H2O)6] three plus, and [Zn(H2O)6] two plus

- Transition metal ions



Ions are [Cr(h2O)6] three plus, [Fe(H2O)6] two plus, [Co(H2O)6] two plus, [Ni(H2O)6] two plus, and [Cu[H2O)6] two plus.

The corresponding transition metal ions are colored. Some, like the hexaaquamanganese(II) ion (not shown) and the hexaaquairon(II) ion, are quite faintly colored - but they are colored.

So, what causes transition metal ions to absorb wavelengths from visible light (causing color) whereas non-transition metal ions do not? And why does the color vary so much from ion to ion? This is discussed in the next sections.

Magnetism

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism. Only the first two are introduced below.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can spin in either direction, they display magnetic moments in any direction. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (described via molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

A chemical demonstration of the paramagnetism of oxygen, as shown by the attraction of liquid oxygen to a magnet. Carleton University, Ottawa, Canada.

As shown in the video, molecular oxygen (O_2 is paramagnetic and is attracted to the magnet. Incontrast, Molecular nitrogen, N_2 , however, has no unpaired electrons and it is diamagnetic (this concept is discussed below); it is therefore unaffected by the magnet.

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include Sc^{3+}, Ti^{4+}, Zn^{2+}, and Cu^{+}. These metals are the not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 23.5.6.

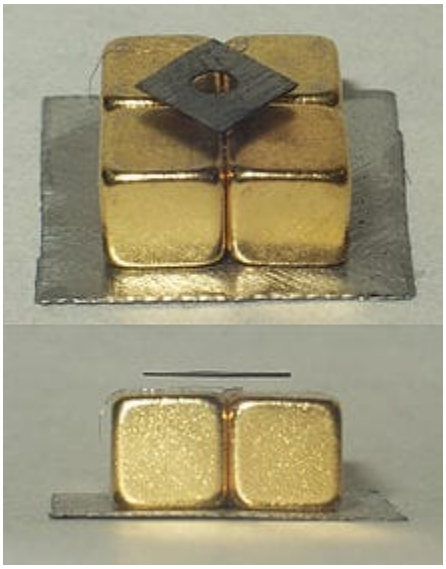


Figure 23.5.6: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

How to Tell if a Substance is Paramagnetic or Diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration
2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic (one or more unpaired electrons) or diamagnetic (all electrons paired)

Example 23.5.4: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

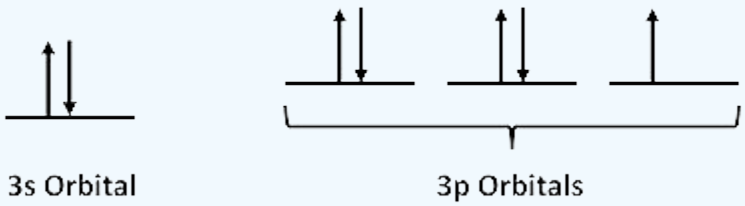
Solution

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

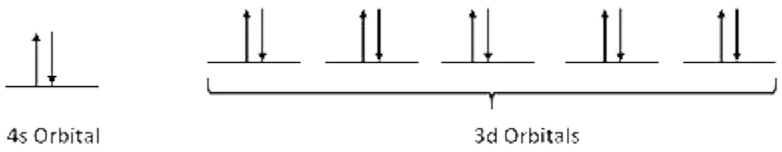
Since there is an unpaired electron, Cl atoms are paramagnetic (but is quite weak).

Example 2: Zinc Atoms

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^2 3d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

References

1. Pettrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007
2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

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23.6: Crystal Field Theory

Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

d-Orbital Splittings

CFT focuses on the interaction of the five (n – 1)d orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure $23.6.1a$). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure $23.6.1b$, the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the e_g orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (d_{xy}, d_{xz}, and d_{yz}, collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

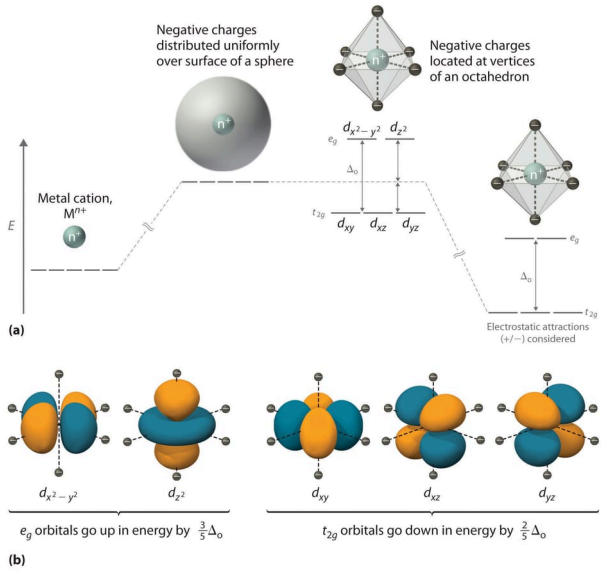


Figure 23.6.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the, d_{xy}, d_{xz}, and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two e_g orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: Δ_t.) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two e_g orbitals increase in energy by $0.6\Delta_o$, whereas the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0.$$

Crystal field splitting does not change the total energy of the d orbitals.

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 23.6.1*a*).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 23.6.1 to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 24.6.2, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

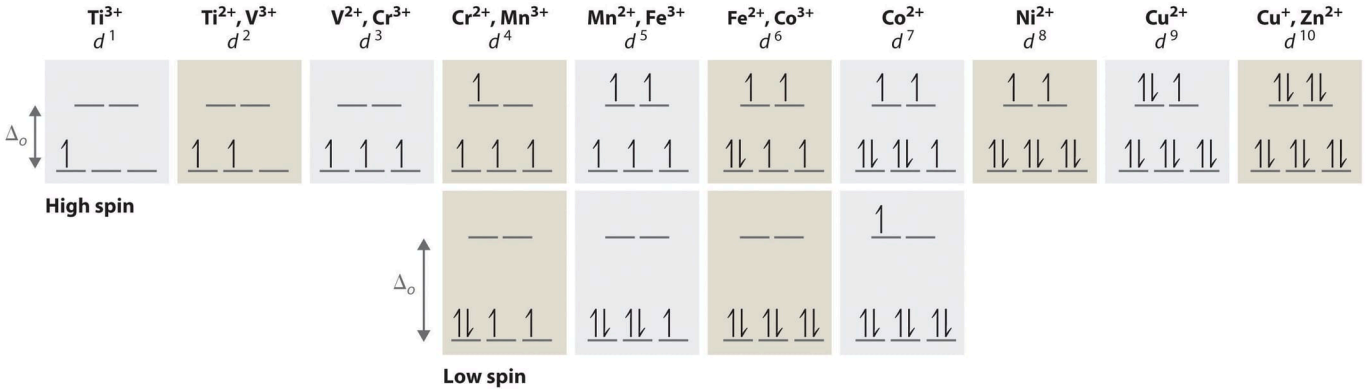


Figure 23.6.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed.

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupied t_{2g} orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e_g orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of d electrons is possible for metal ions with d^8–d^{10} electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

> If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table 23.6.1.

Table 23.6.1: Crystal Field Splitting Energies for Some Octahedral (Δ_o) and Tetrahedral (Δ_t) Transition-Metal Complexes*

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300

***Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.**

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

***Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.**

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}: \Delta_o = 22{,}900\ cm^{-1}$$

$$[Rh(NH_3)_6]^{3+}: \Delta_o = 34{,}100\ cm^{-1}$$

$$[Ir(NH_3)_6]^{3+}: \Delta_o = 40{,}000\ cm^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter

M–L distances and stronger d orbital–ligand interactions.

The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order $F^- > Cl^- > Br^- > I-$ because smaller, more localized charges, such as we see for F^-, interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$\underset{\text{strong-field ligands}}{\mathrm{CO} \approx \mathrm{CN}^- > \mathrm{NO}_2^-} > \mathrm{en} > \mathrm{NH_3} > \underset{\text{intermediate-field ligands}}{\mathrm{SCN}^- > \mathrm{H_2O}} > \mathrm{oxalate}^{2-} > \mathrm{OH}^- > \mathrm{F} > \mathrm{acetate}^- > \underset{\text{weak-field ligands}}{\mathrm{Cl}^- > \mathrm{Br}^- > \mathrm{I}^-}$$

The values of Δ_o listed in Table $23.6.1$ illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

> The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.

Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a d–d transition (Figure 24.6.3). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o.

Figure $23.6.3$: A d–d Transition. In a d–d transition, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o. Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of Cr^{3+} impurities in octahedral sites in an otherwise colorless metal oxide lattice.

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 23.6.2 gives CFSE values for octahedral complexes with different d electron configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table 23.6.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
d^0			0			
d^1	↑		0.4			
d^2	↑ ↑		0.8			
d^3	↑ ↑ ↑		1.2			
d^4	↑ ↑ ↑	↑	0.6	↑↓ ↑ ↑		1.6
d^5	↑ ↑ ↑	↑ ↑	0.0	↑↓ ↑↓ ↑		2.0
d^6	↑↓ ↑ ↑	↑ ↑	0.4	↑↓ ↑↓ ↑↓		2.4
d^7	↑↓ ↑↓ ↑	↑ ↑	0.8	↑↓ ↑↓ ↑↓	↑	1.8
d^8	↑↓ ↑↓ ↑↓	↑ ↑	1.2			
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	0.6			

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
d^{10}	↿⇂ ↿⇂ ↿⇂	↿⇂ ↿⇂	0.0			

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.

Example 23.6.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[CoF_6]^{3-}$
b. $[Rh(CO)_2Cl_2]^-$

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

a. From the number of ligands, determine the coordination number of the compound.
b. Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.
c. Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.
d. Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

Solution

a. A With six ligands, we expect this complex to be octahedral.

   B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

   C Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

   D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

   B C Because rhodium is a second-row transition metal ion with a d^8 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order $d_{z^2}d_{yz}$, and d_{xz} (these are degenerate); d_{xy}; and $d_{x^2-y^2}$.

   D The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2-y^2}$. orbital empty. Thus there are no unpaired electrons.

Exercise 23.6.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[Mn(H_2O)_6]^{2+}$
b. $[PtCl_4]^{2-}$

Answers

a. octahedral; high spin; five
b. square planar; low spin; no unpaired electrons

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

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23.E: Chemistry of Coordination Chemistry (Exercises)

Questions migrated to ADAPT

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24: CHEMISTRY OF LIFE- ORGANIC AND BIOLOGICAL CHEMISTRY

Carbon is unique among the elements in its ability to *catenate*, to form a wide variety of compounds that contain long chains and/or rings of carbon atoms. Some of the most complex chemical structures known are those of the organic molecules found in living organisms. In spite of their size and complexity, these biological molecules obey the same chemical principles as simpler organic molecules. Thus we can use Lewis electron structures to understand the preferred mode of reactivity of a variety of organic compounds, relative electronegativities and bond polarities to predict how certain groups of atoms will react, and molecular orbital theory to explain why certain organic species that contain multiple bonds are especially stable or undergo particular reactions when they interact with light.

In this chapter, we continue our description of organic compounds by focusing on their molecular structures and reactivity; we will also introduce some of the fundamental types of reactions and reaction mechanisms you will encounter in organic and biological chemistry. We discuss why butter is a solid and oils are liquids despite the apparent similarities in their structures, why the widely used anti-inflammatory drug ibuprofen takes longer than half an hour to relieve pain, and the identity of the major carcinogen in grilled meats and cigarette smoke. The chapter concludes with a brief introduction to the molecules of life, which will explain how the consumption of lactose can result in mental retardation and cirrhosis of the liver in some individuals, how hibernating animals survive during the winter, and how certain groups of antibiotics kill bacteria that are harmful to humans.

24.1: General Characteristics of Organic Molecules

24.2: Introduction to Hydrocarbons

24.3: Alkanes

24.4: Unsaturated Hydrocarbons

24.5: Functional Groups

24.6: Compounds with a Carbonyl Group

24.7: Chirality in Organic Chemistry

24.8: Introduction to Biochemistry

24.9: Proteins

24.10: Carbohydrates

24.11: Nucleic Acids

24.E: Organic and Biological Chemistry (Exercises)

24.S: Organic and Biological Chemistry (Summary)

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24.1: General Characteristics of Organic Molecules

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

Organic substances have been used throughout this text to illustrate the differences between ionic and covalent bonding and to demonstrate the intimate connection between the structures of compounds and their chemical reactivity. You learned, for example, that even though NaOH and alcohols (ROH) both have OH in their formula, NaOH is an ionic compound that dissociates completely in water to produce a basic solution containing Na^+ and OH^- ions, whereas alcohols are covalent compounds that do not dissociate in water and instead form neutral aqueous solutions. You also learned that an amine (RNH_2), with its lone pairs of electrons, is a base, whereas a carboxylic acid (RCO_2H), with its dissociable proton, is an acid.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{24.1.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today **organic chemistry** is the study of the chemistry of the carbon compounds, and **inorganic chemistry** is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 24.1.1.

Table 24.1.1: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane	Inorganic	NaCl
low melting points	–95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C

Organic	Hexane	Inorganic	NaCl
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table 24.1.1 also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table 24.1.1.

Key Takeaway

- Organic chemistry is the study of carbon compounds, nearly all of which also contain hydrogen atoms.

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24.2: Introduction to Hydrocarbons

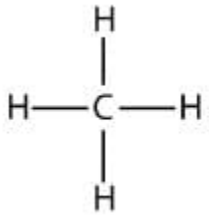
Learning Objectives

- To get an overview of hydrocarbons molecules and their four primary classifications

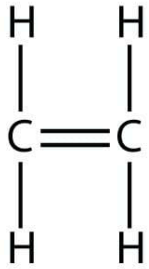
Hydrocarbons are organic compounds that contain **only** carbon and hydrogen. The four general classes of hydrocarbons are: alkanes, alkenes, alkynes and arenes. Aromatic compounds derive their names from the fact that many of these compounds in the early days of discovery were grouped because they were oils with fragrant odors.

The classifications for hydrocarbons, defined by IUPAC nomenclature of organic chemistry are as follows:

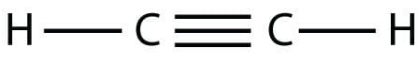
1. Saturated hydrocarbons (alkanes) are the simplest of the hydrocarbon species. They are composed entirely of single bonds and are saturated with hydrogen. The general formula for saturated hydrocarbons is C_nH_{2n+2} (assuming non-cyclic structures). Saturated hydrocarbons are the basis of petroleum fuels and are found as either linear or branched species.The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:



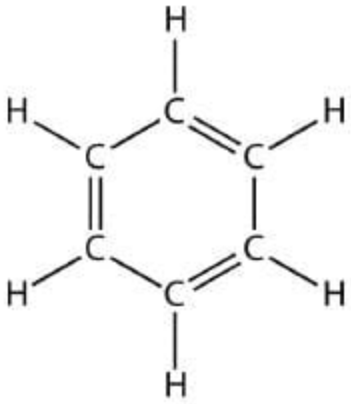
2. Unsaturated hydrocarbons have one or more double or triple bonds between carbon atoms. Those with double bond are called alkenes and those with one double bond have the formula C_nH_{2n} (assuming non-cyclic structures). Those containing triple bonds are called alkynes, with general formula C_nH_{2n-2}. The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:



The smallest alkyne is ethyne, which is also known as acetylene:



3. Cycloalkanes are hydrocarbons containing one or more carbon rings to which hydrogen atoms are attached. The general formula for a saturated hydrocarbon containing one ring is C_nH_{2n}.
4. Aromatic hydrocarbons, also known as arenes, are hydrocarbons that have at least one aromatic ring. Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double C–C bonds:



Because of differences in molecular structure, the empirical formula remains different between hydrocarbons; in linear, or "straight-run" alkanes, alkenes and alkynes, the amount of bonded hydrogen lessens in alkenes and alkynes due to the "self-bonding" or catenation of carbon preventing entire saturation of the hydrocarbon by the formation of double or triple bonds.

The inherent ability of hydrocarbons to bond to themselves is known as catenation, and allows hydrocarbon to form more complex molecules, such as cyclohexane, and in rarer cases, arenes such as benzene. This ability comes from the fact that the bond character between carbon atoms is entirely non-polar, in that the distribution of electrons between the two elements is somewhat even due to the same electronegativity values of the elements (~0.30).

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24.3: Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). S*aturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure 24.3.1.

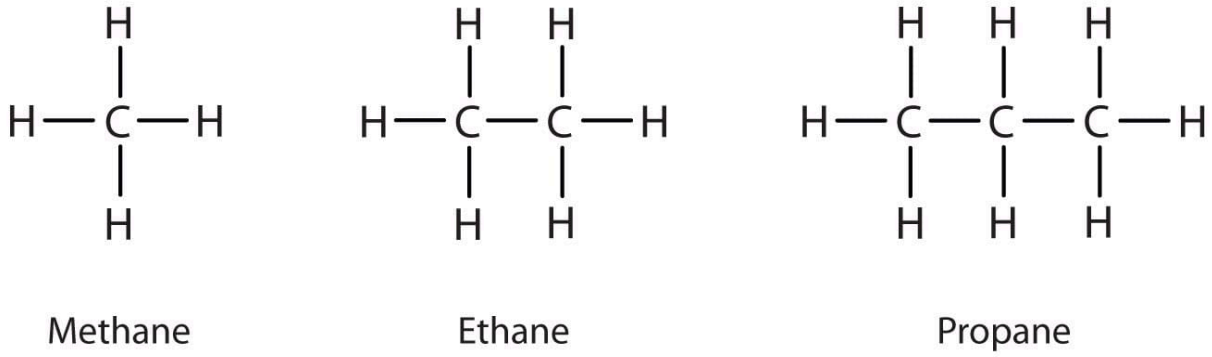


Figure 24.3.1: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure 24.3.2).

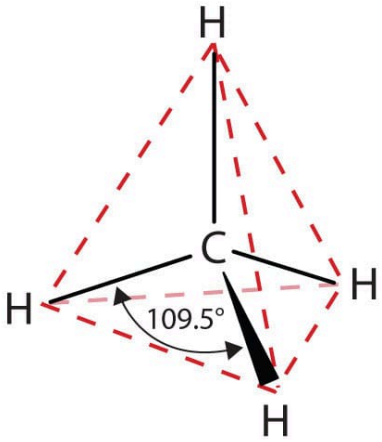


Figure 24.3.2: The Tetrahedral Methane Molecule

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table 24.3.1.

Table 24.3.1: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure 24.3.3. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

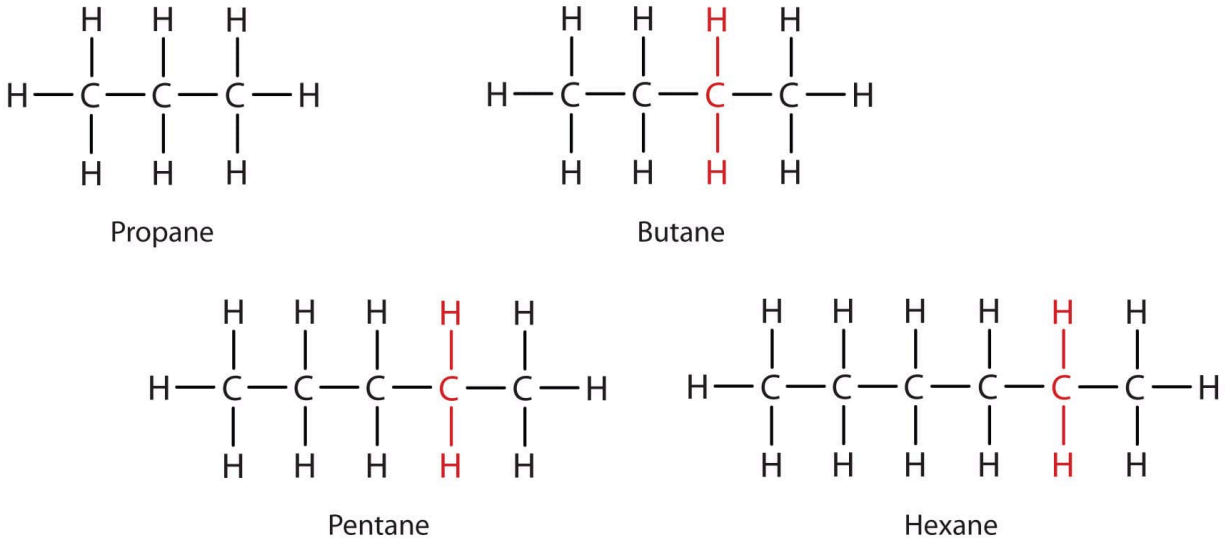


Figure 24.3.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: $C_nH_{2n + 2}$. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8) + 2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

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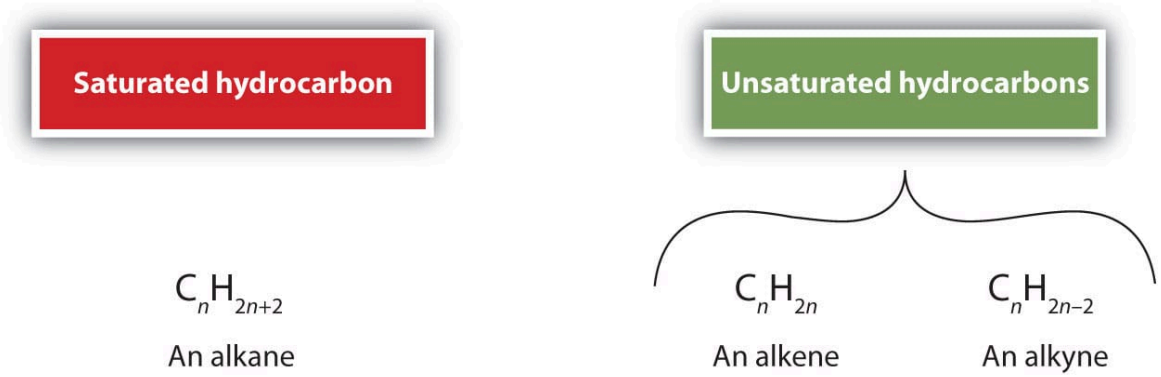
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24.4: Unsaturated Hydrocarbons

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

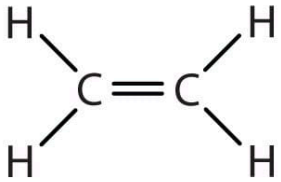


Some representative alkenes—their names, structures, and physical properties—are given in Table 24.4.1.

Table 24.4.1: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2{=}CH_2$	−169	−104
propene	C_3H_6	$CH_2{=}CHCH_3$	−185	−47
1-butene	C_4H_8	$CH_2{=}CHCH_2CH_3$	−185	−6
1-pentene	C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	−138	30
1-hexene	C_6H_{12}	$CH_2{=}CH(CH_2)_3CH_3$	−140	63
1-heptene	C_7H_{14}	$CH_2{=}CH(CH_2)_4CH_3$	−119	94
1-octene	C_8H_{16}	$CH_2{=}CH(CH_2)_5CH_3$	−102	121

We used only condensed structural formulas in Table 24.4.1. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does

not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table 24.4.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 24.4.1). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

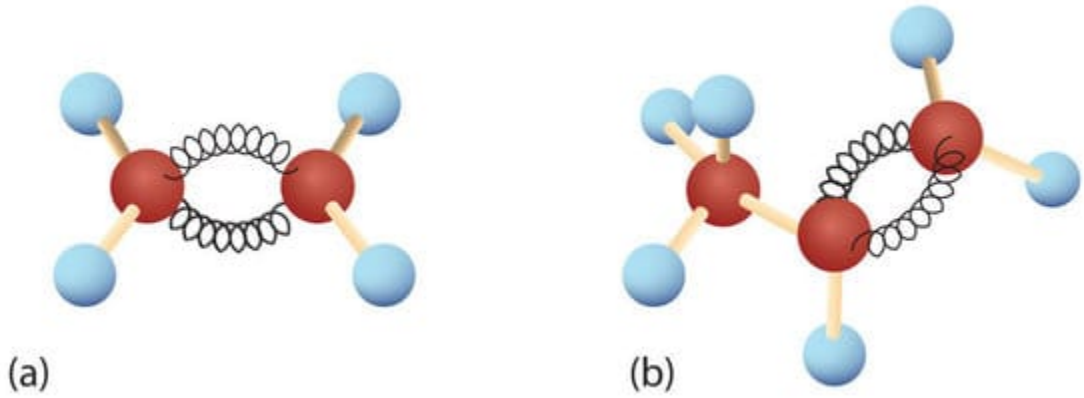
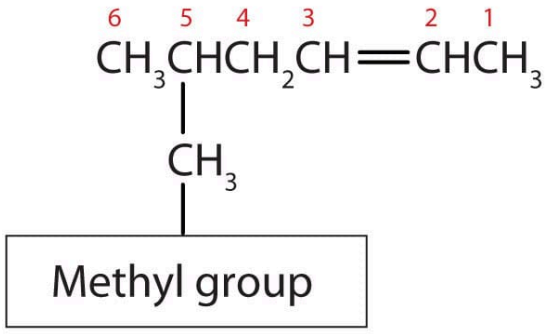


Figure 24.4.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

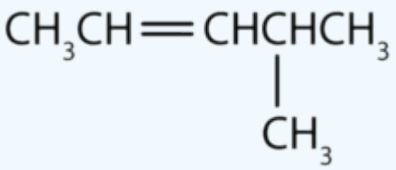
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

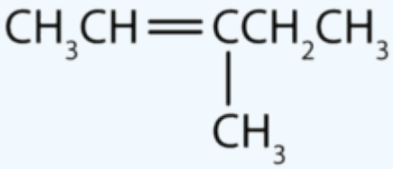
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound $CH_2{=}CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound $CH_3CH{=}CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



Example 24.4.1

Name each compound.

a. 

b. 

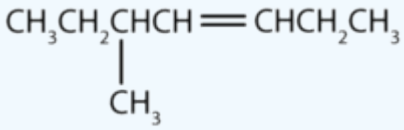
Solution

a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

Exercise 24.4.1

Name each compound.

a. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$

b. 

Answer available at the end of this section.

Example 24.4.2

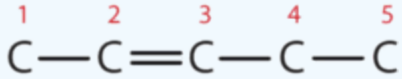
Draw the structure for each compound.

a. 3-methyl-2-pentene
b. cyclohexene

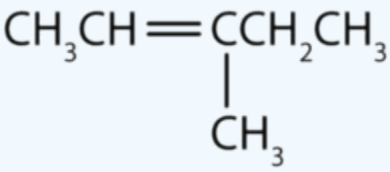
Solution

a.

First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:

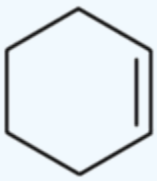


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



Exercise 24.4.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

Answers

Exercise 24.4.1

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

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24.5: Functional Groups

Learning Objectives

- To know the major classes of organic compounds and identify important functional groups.

You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). The major families of organic compounds are characterized by their functional groups. Figure 24.5.1 summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

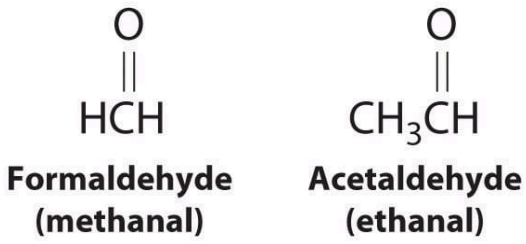
Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	$RC{\equiv}CR'$	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH^a		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX^a		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH^a	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	$ArOH^a$		phenol	-ol
Ethers	ROR'	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	RCHO		acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	$RR'C{=}O$		acetone (2-propanone)	-one
Carboxylic acids	RCO_2H		acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO_2R'		methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	$RCONHR'$		*N*-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH_2, $RNHR'$, $RNR'R''$	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC{\equiv}N$	$H_3CC{\equiv}N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2^a$		nitrobenzene	nitro-

[a]R indicates an alkyl group; Ar indicates an *aryl* group.

Figure 24.5.1: Major Classes of Organic Compounds

The first family listed in Figure 24.5.1 is the hydrocarbons. These include alkanes, with the general molecular formula C_nH_{2n+2} where n is an integer; alkenes, represented by C_nH_{2n}; alkynes, represented by C_nH_{2n-2}; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the $–CO_2H$ functional group is replaced by either an alkoxy (–OR) group, producing an ester, or by an amido (–NRR′, where R and R′ can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a C≡N bond; and nitro compounds, which contain the $–NO_2$ group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2C{=}O$]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.



Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first CH_3 group in dimethyl benzene is indicated with a 1, but the second CH_3 group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure 24.5.2). In common nomenclature, in contrast, the prefixes ortho-, meta-, and para- are used to describe the relative positions of groups attached to an aromatic ring. If the CH_3 groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called ortho-xylene, abbreviated o-xylene. If they are across from each other on the ring, the compound is commonly called para-xylene or p-xylene. When the arrangement is intermediate between those of ortho- and para-compounds, the name is meta-xylene or m-xylene.

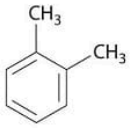
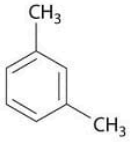
Prefix	Positions of Methyl Groups	Example	Common Name (Systematic Name)
ortho-	1,2		*o*-xylene (1,2-dimethylbenzene)
meta-	1,3		*m*-xylene (1,3-dimethylbenzene)
para-	1,4		*p*-xylene (1,4-dimethylbenzene)

Figure 24.5.2: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

Conceptual Problems

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

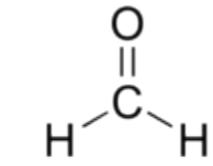
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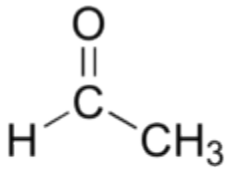
24.6: Compounds with a Carbonyl Group

Aldehydes and Ketones

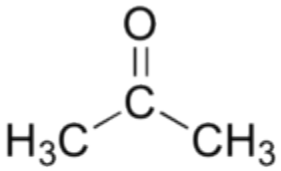
There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.



formaldehyde

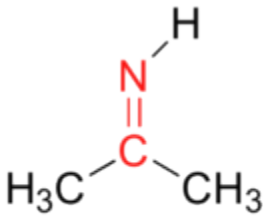


acetaldehyde



acetone
(a ketone)

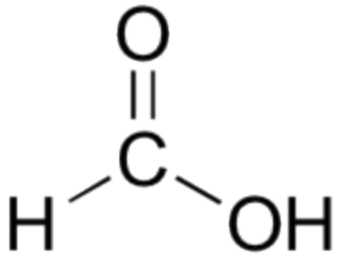
Molecules with carbon-nitrogen double bonds are called **imines**, or **Schiff bases**.



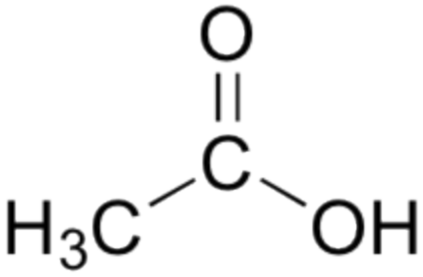
an imine

Carboxylic acids and acid derivatives

If a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to a **heteroatom** (in organic chemistry, this term generally refers to oxygen, nitrogen, sulfur, or one of the halogens), the functional group is considered to be one of the '**carboxylic acid derivatives**', a designation that describes a grouping of several functional groups. The eponymous member of this grouping is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl (OH) group.

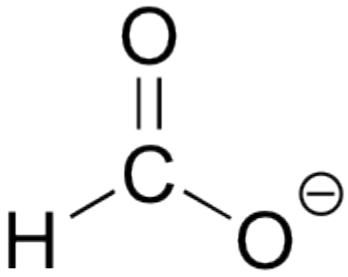


formic acid

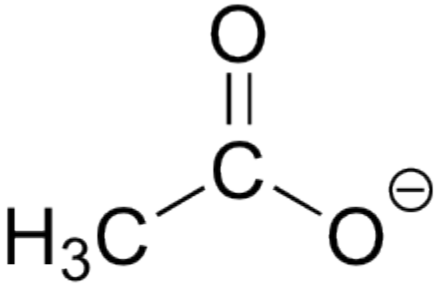


acetic acid
(vinegar)

As the name implies, carboxylic acids are acidic, meaning that they are readily deprotonated to form the conjugate base form, called a **carboxylate** (much more about carboxylic acids in the acid-base chapter!).

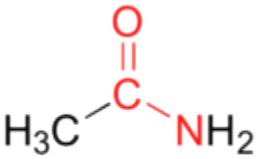


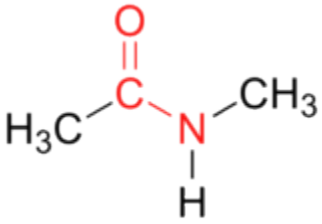
formate

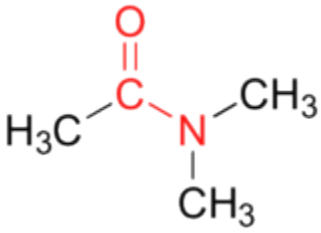


acetate

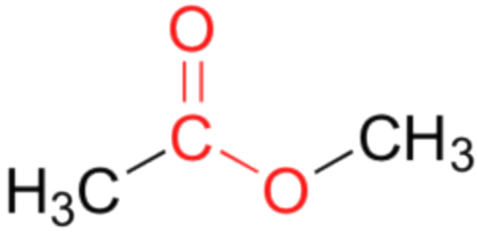
In **amides**, the carbonyl carbon is bonded to a nitrogen. The nitrogen in an amide can be bonded either to hydrogens, to carbons, or to both. Another way of thinking of an amide is that it is a carbonyl bonded to an amine.



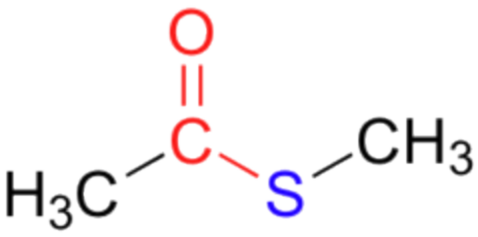




In **esters**, the carbonyl carbon is bonded to an oxygen which is itself bonded to another carbon. Another way of thinking of an ester is that it is a carbonyl bonded to an alcohol. **Thioesters** are similar to esters, except a sulfur is in place of the oxygen.

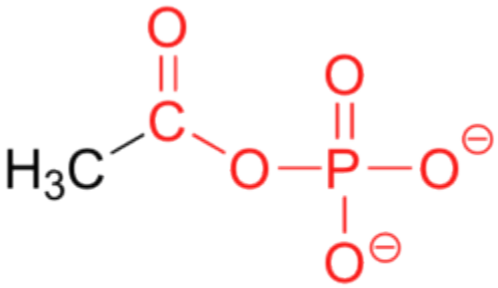


an ester

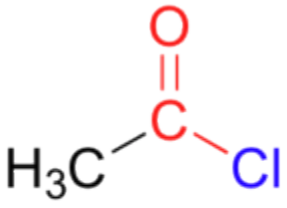


a thioester

In an **acyl phosphate**, the carbonyl carbon is bonded to the oxygen of a phosphate, and in an **acid chloride**, the carbonyl carbon is bonded to a chlorine.

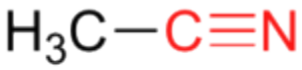


an acyl phosphate



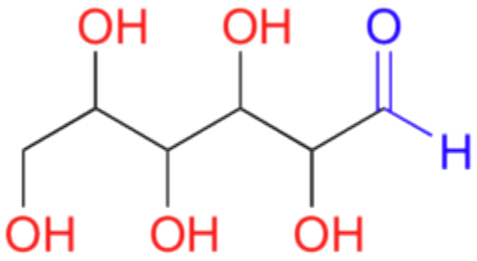
an acid chloride

Finally, in a **nitrile** group, a carbon is triple-bonded to a nitrogen. Nitriles are also often referred to as **cyano** groups.

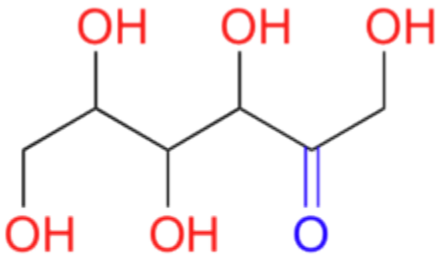


a nitrile

A single compound often contains several functional groups. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').

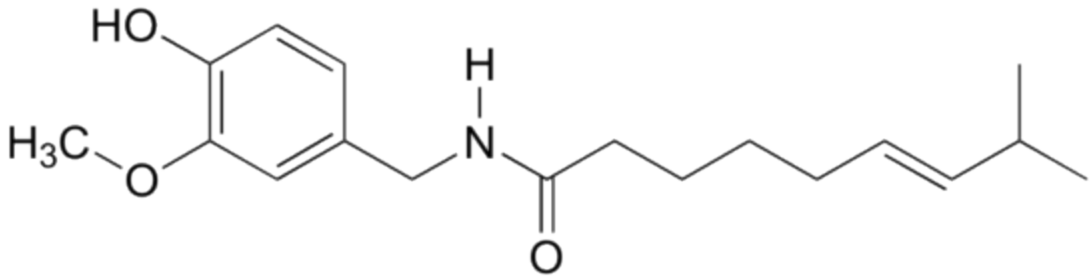


glucose



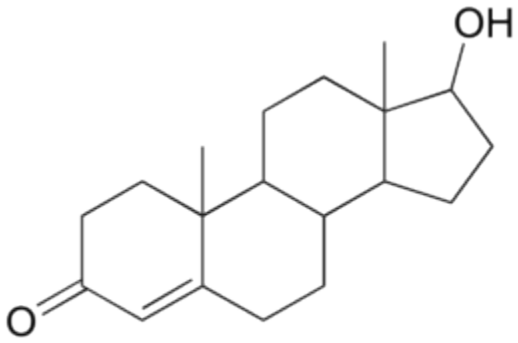
fructose

Capsaicin, the compound responsible for the heat in hot peppers, contains phenol, ether, amide, and alkene functional groups.

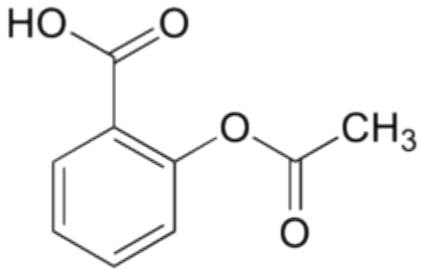


capsiacin

The male sex hormone testosterone contains ketone, alkene, and secondary alcohol groups, while acetylsalicylic acid (aspirin) contains aromatic, carboxylic acid, and ester groups.



testosterone



acetylsalicylic acid
(aspirin)

While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological and laboratory organic chemistry. The table on the inside back cover provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

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24.7: Chirality in Organic Chemistry

Organic compounds, molecules created around a chain of carbon atom (more commonly known as carbon backbone), play an essential role in the chemistry of life. These molecules derive their importance from the energy they carry, mainly in a form of potential energy between atomic molecules. Since such potential force can be widely affected due to changes in atomic placement, it is important to understand the concept of an isomer, a molecule sharing same atomic make up as another but differing in structural arrangement.

Stereoisomers are isomers that differ in spatial arrangement of atoms, rather than order of atomic connectivity. One of their most interesting type of isomer is the mirror-image stereoisomers, a non-superimposable set of two molecules that are mirror image of one another. The existence of these molecules are determined by concept known as chirality.

Stereoisomers

Molecules with the same connectivity but different arrangements of the atoms in space are called stereoisomers. There are two types of stereoisomers: geometric and optical. Geometric isomers differ in the relative position(s) of substituents in a rigid molecule. Simple rotation about a C–C σ bond in an alkene, for example, cannot occur because of the presence of the π bond. The substituents are therefore rigidly locked into a particular spatial arrangement. Thus a carbon–carbon multiple bond, or in some cases a ring, prevents one geometric isomer from being readily converted to the other. The members of an isomeric pair are identified as either cis or trans, and interconversion between the two forms requires breaking and reforming one or more bonds. Because their structural difference causes them to have different physical and chemical properties, cis and trans isomers are actually two distinct chemical compounds.

> Stereoisomers have the same connectivity, but different arrangements of atoms in space.

Optical isomers are molecules whose structures are mirror images but cannot be superimposed on one another in any orientation. Optical isomers have identical physical properties, although their chemical properties may differ in asymmetric environments. Molecules that are nonsuperimposable mirror images of each other are said to be chiral (pronounced “ky-ral,” from the Greek cheir, meaning “hand”). Examples of some familiar chiral objects are your hands, feet, and ears. As shown in Figure $24.7.1a$, your left and right hands are nonsuperimposable mirror images. (Try putting your right shoe on your left foot—it just doesn’t work.) An achiral object is one that can be superimposed on its mirror image, as shown by the superimposed flasks in Figure $24.7.1b$.

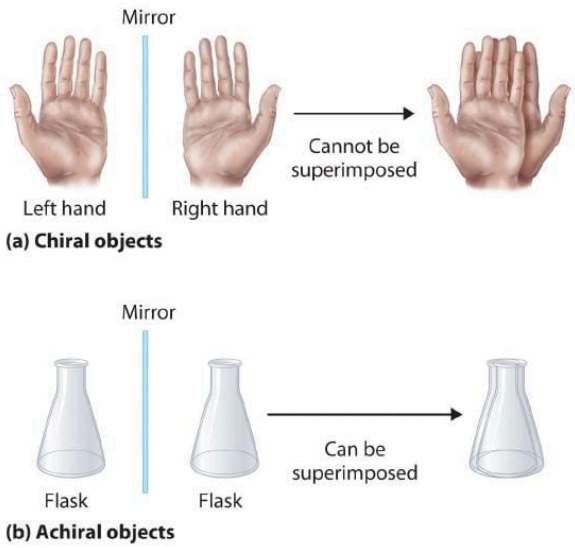


Figure $24.7.1$: Chiral and Achiral Objects. (a) Objects that are nonsuperimposable mirror images of each other are chiral, such as the left and the right hand. (b) The unmarked flask is achiral because it can be superimposed on its mirror image.

Most chiral organic molecules have at least one carbon atom that is bonded to four different groups, as occurs in the

bromochlorofluoromethane molecule shown in part (a) in Figure 24.7.2. This carbon, often designated by an asterisk in structural drawings, is called a chiral center or asymmetric carbon atom. If the bromine atom is replaced by another chlorine (Figure 24.7.2*b*), the molecule and its mirror image can now be superimposed by simple rotation. Thus the carbon is no longer a chiral center. Asymmetric carbon atoms are found in many naturally occurring molecules, such as lactic acid, which is present in milk and muscles, and nicotine, a component of tobacco. A molecule and its nonsuperimposable mirror image are called enantiomers (from the Greek enantiou, meaning “opposite”).

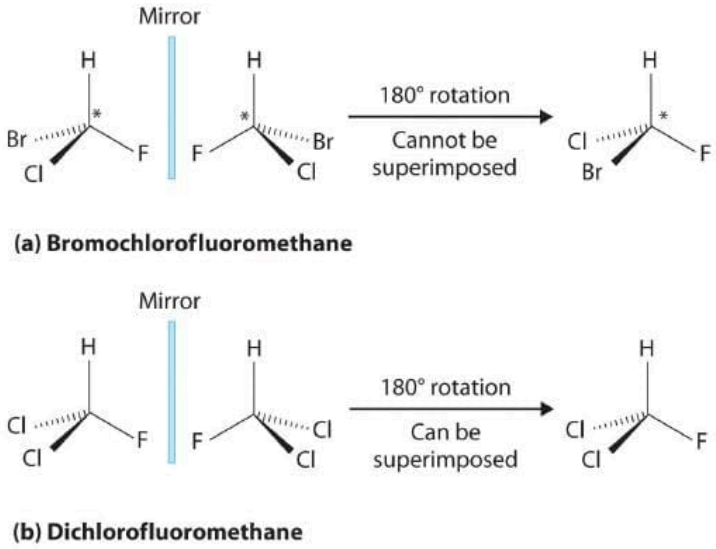
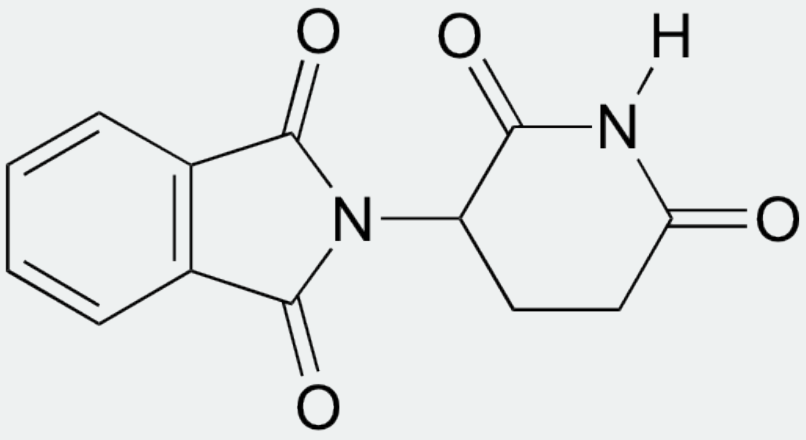


Figure 24.7.2: Comparison of Chiral and Achiral Molecules. (a) Bromochlorofluoromethane is a chiral molecule whose stereocenter is designated with an asterisk. Rotation of its mirror image does not generate the original structure. To superimpose the mirror images, bonds must be broken and reformed. (b) In contrast, dichlorofluoromethane and its mirror image can be rotated so they are superimposable.

Thalidomide

In the 1960’s, a drug called thalidomide was widely prescribed in the Western Europe to alleviate morning sickness in pregnant women.



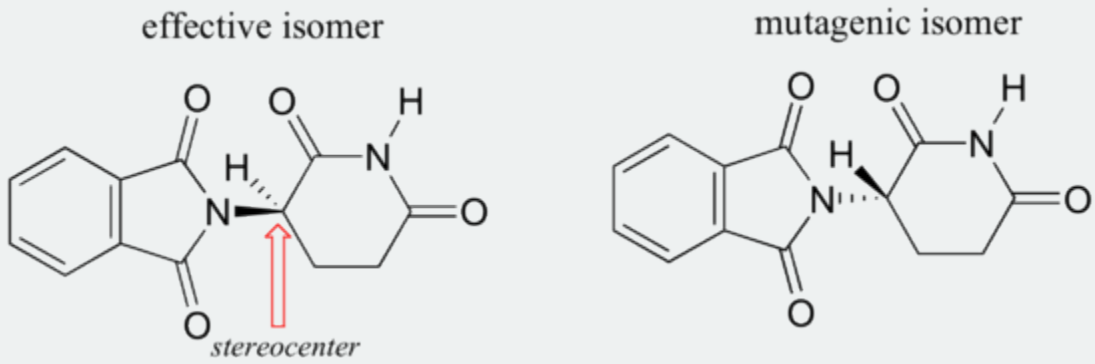
thalidomide

Thalidomide had previously been used in other countries as an antidepressant, and was believed to be safe and effective for both purposes. The drug was not approved for use in the U.S.A. It was not long, however, before doctors realized that something had gone horribly wrong: many babies born to women who had taken thalidomide during pregnancy suffered from severe birth defects.



Baby born to a mother who had taken thalidomide while pregnant.

Researchers later realized the that problem lay in the fact that thalidomide was being provided as a mixture of two different isomeric forms.



One of the isomers is an effective medication, the other caused the side effects. Both isomeric forms have the same molecular formula and the same atom-to-atom connectivity, so they are not constitutional isomers. Where they differ is in the arrangement in three-dimensional space about one tetrahedral, sp^3-hybridized carbon. These two forms of thalidomide are **stereoisomers**.

Looking for planes of symmetry in a molecule is useful, but often difficult in practice. In most cases, the easiest way to decide whether a molecule is chiral or achiral is to look for one or more stereocenters - with a few rare exceptions, the general rule is that molecules with at least one stereocenter are chiral, and molecules with no stereocenters are achiral. Carbon stereocenters are also referred to quite frequently as **chiral carbons**.

When evaluating a molecule for chirality, it is important to recognize that the question of whether or not the dashed/solid wedge drawing convention is used is irrelevant. Chiral molecules are sometimes drawn without using wedges (although obviously this means that stereochemical information is being omitted). Conversely, wedges may be used on carbons that are not stereocenters – look, for example, at the drawings of glycine and citrate in the figure above. Just because you see dashed and solid wedges in a structure, do not automatically assume that you are looking at a stereocenter.

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24.8: Introduction to Biochemistry

Biochemistry is the study of chemical processes in living organisms, including, but not limited to, living matter. Biochemistry governs all living organisms and living processes. By controlling information flow through biochemical signaling and the flow of chemical energy through metabolism, biochemical processes give rise to the incredible complexity of life.

Over the last decades of the 20th century, biochemistry become so successful at explaining living processes that now almost all areas of the life sciences from botany to medicine to genetics are engaged in biochemical research. Today, the main focus of pure biochemistry is in understanding how biological molecules give rise to the processes that occur within living cells, which in turn relates greatly to the study and understanding of whole organisms.

Biochemistry is closely related to molecular biology, the study of the molecular mechanisms by which genetic information encoded in DNA is able to result in the processes of life. Depending on the exact definition of the terms used, molecular biology can be thought of as a branch of biochemistry, or biochemistry as a tool with which to investigate and study molecular biology.

Much of biochemistry deals with the structures, functions and interactions of biological macromolecules, such as proteins, nucleic acids, carbohydrates and lipids, which provide the structure of cells and perform many of the functions associated with life. The chemistry of the cell also depends on the reactions of smaller molecules and ions. These can be inorganic, for example water and metal ions, or organic, for example the amino acids which are used to synthesize proteins. The mechanisms by which cells harness energy from their environment via chemical reactions are known as metabolism. The findings of biochemistry are applied primarily in medicine, nutrition, and agriculture. In medicine, biochemists investigate the causes and cures of disease. In nutrition, they study how to maintain health and study the effects of nutritional deficiencies. In agriculture, biochemists investigate soil and fertilizers, and try to discover ways to improve crop cultivation, crop storage and pest control. Much of biochemistry deals with the structures and functions of cellular components such as proteins, carbohydrates, lipids, nucleic acids and other biomolecules—although increasingly processes rather than individual molecules are the main focus.

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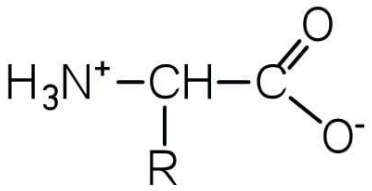
24.9: Proteins

Learning Objectives

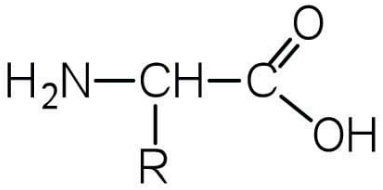
- To recognize amino acids and classify them based on the characteristics of their side chains.

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 amino acids, so called because each contains an amino group attached to a carboxylic acid. The amino acids in proteins are α-amino acids, which means the amino group is attached to the α-carbon of the carboxylic acid. Humans can synthesize only about half of the needed amino acids; the remainder must be obtained from the diet and are known as essential amino acids. However, two additional amino acids have been found in limited quantities in proteins: Selenocysteine was discovered in 1986, while pyrrolysine was discovered in 2002.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of inorganic salts than those of amines or organic acids and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a zwitterion.



α-Amino acid drawn as a zwitterion



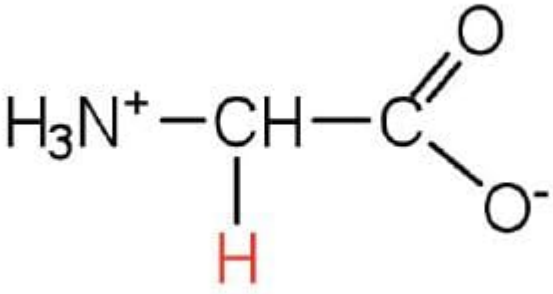
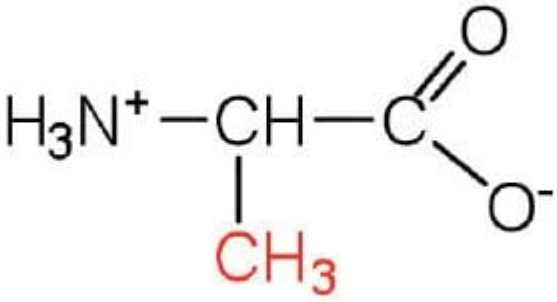
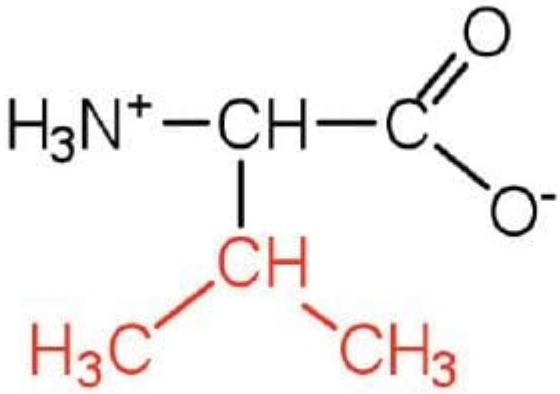
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

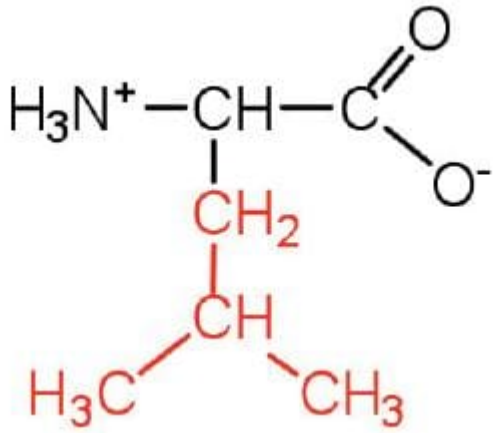
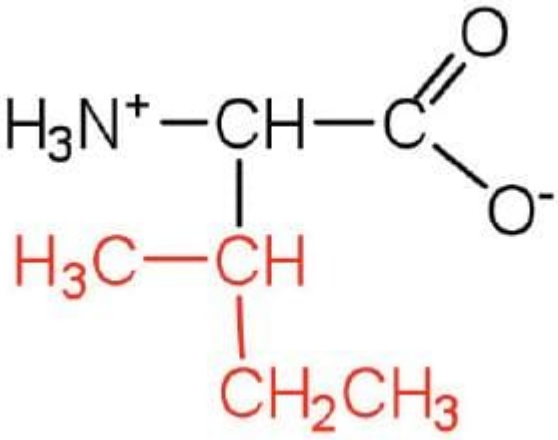
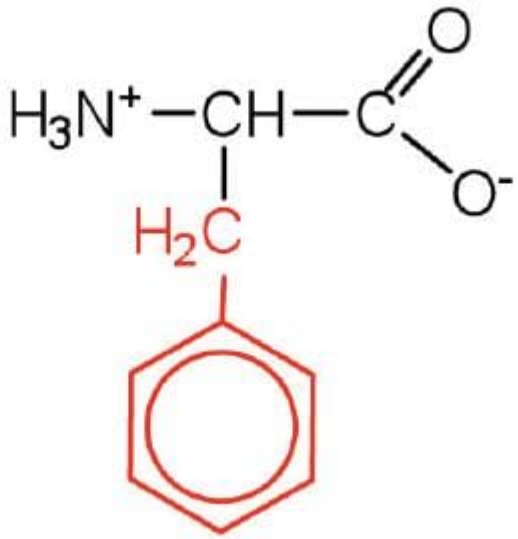
Classification

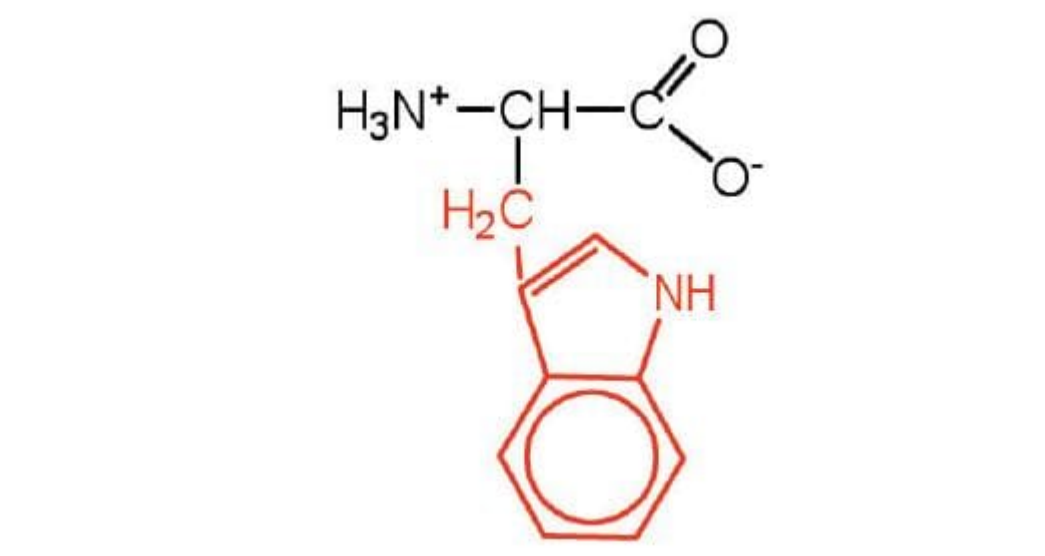
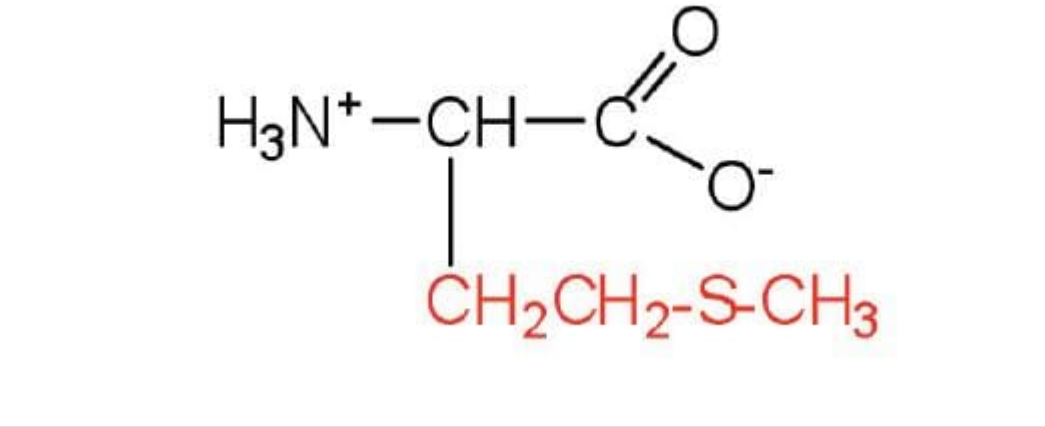
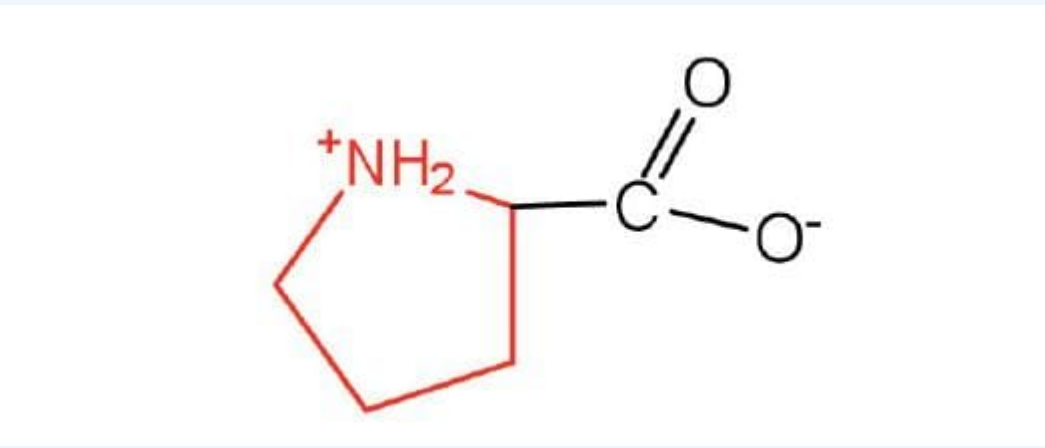
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound effect on the structure and biological activity of proteins. Although amino acids can be classified in various ways, one common approach is to classify them according to whether the functional group on the side chain at neutral pH is nonpolar, polar but uncharged, negatively charged, or positively charged. The structures and names of the 20 amino acids, their one- and three-letter abbreviations, and some of their distinctive features are given in Table 24.9.1.

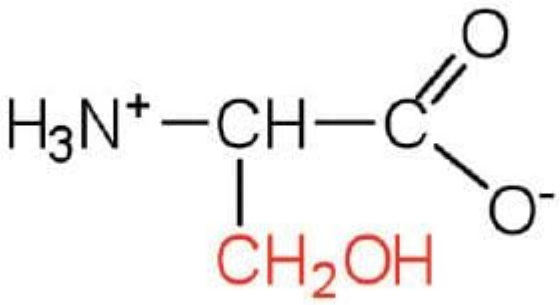
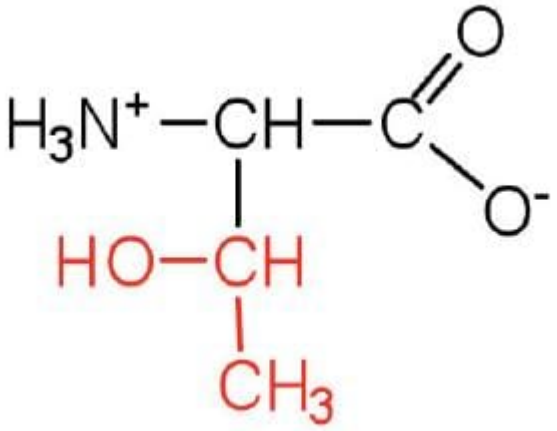
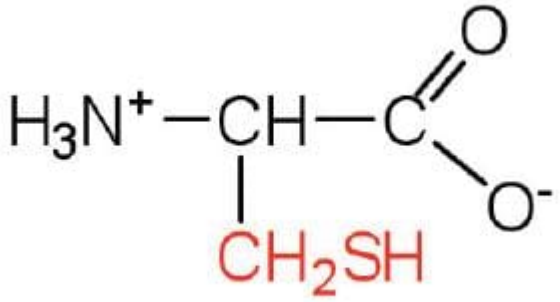
Table 24.9.1: Common Amino Acids Found in Proteins

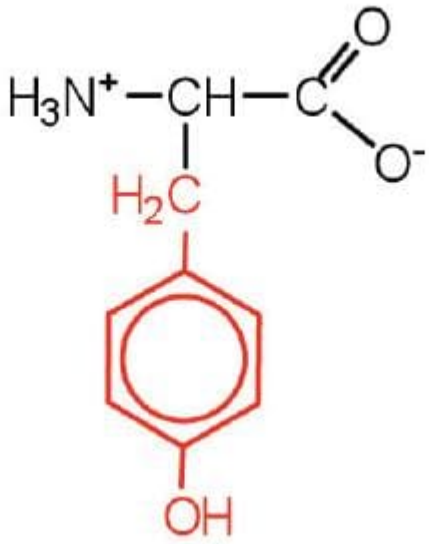
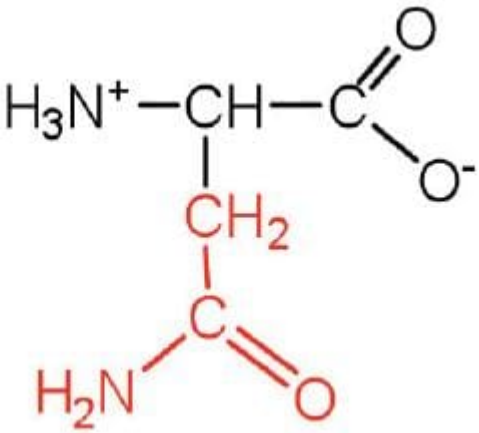
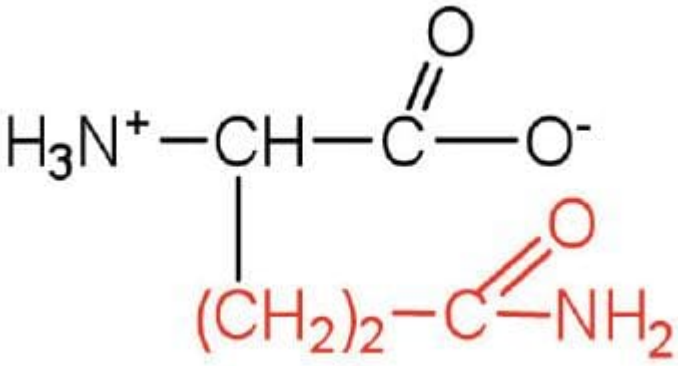
Common Name	Abbreviation	Structural Formula (at pH 6)
		Amino acids with a nonpolar R group

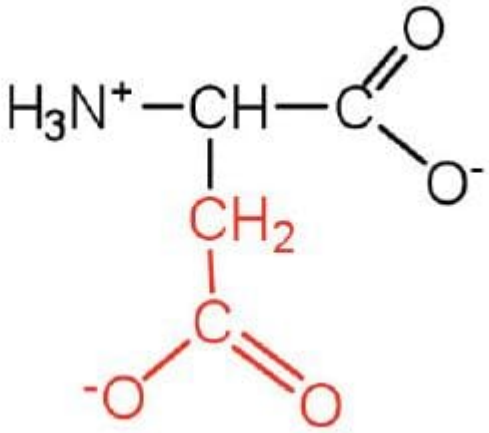
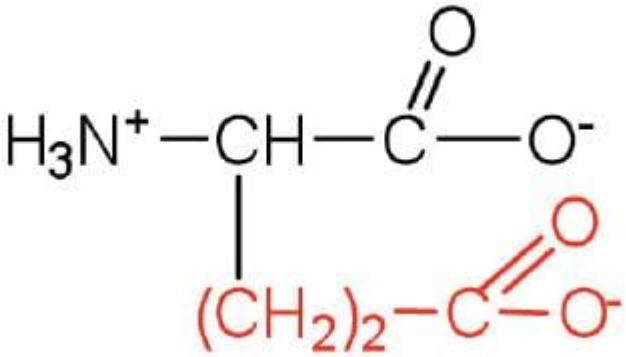
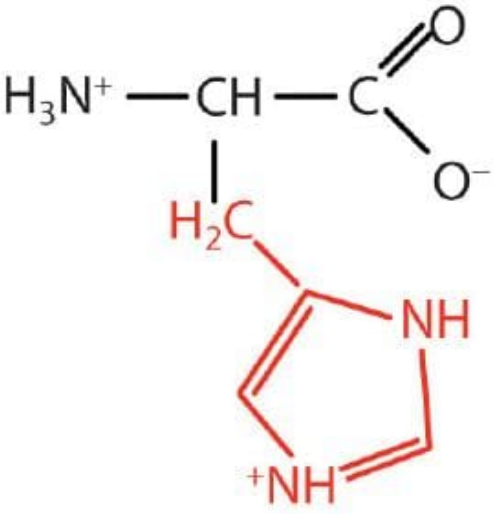
Common Name	Abbreviation	Structural Formula (at pH 6)
glycine	gly (G)	
alanine	ala (A)	
valine	val (V)	

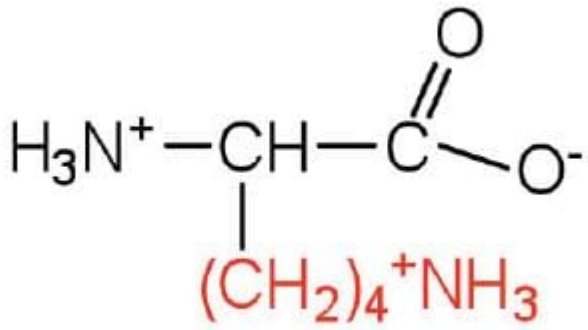
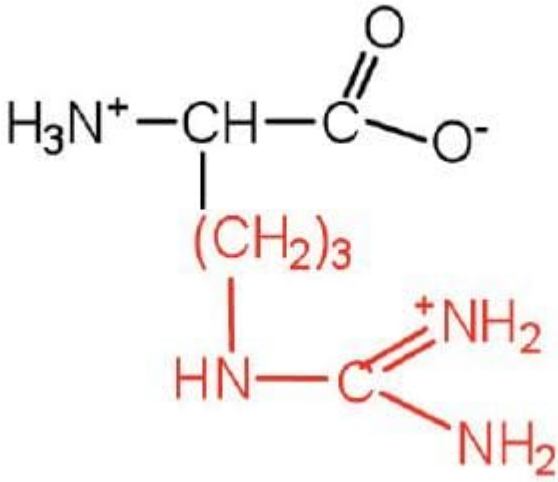
Common Name	Abbreviation	Structural Formula (at pH 6)
leucine	leu (L)	
isoleucine	ile (I)	
phenylalanine	phe (F)	

Common Name	Abbreviation	Structural Formula (at pH 6)
tryptophan	trp (W)	
methionine	met (M)	
proline	pro (P)	
		Amino acids with a polar but neutral R group

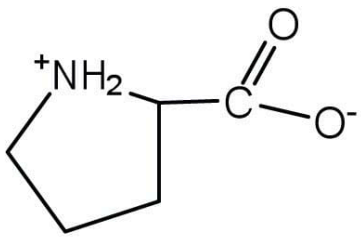
Common Name	Abbreviation	Structural Formula (at pH 6)
serine	ser (S)	
threonine	thr (T)	
cysteine	cys (C)	

Common Name	Abbreviation	Structural Formula (at pH 6)
tyrosine	tyr (Y)	
asparagine	asn (N)	
glutamine	gln (Q)	
		Amino acids with a negatively charged R group

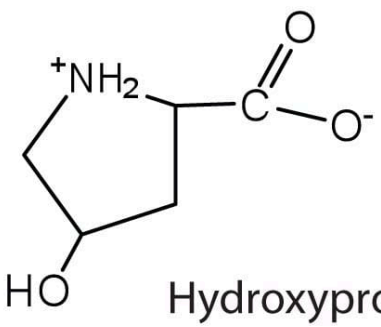
Common Name	Abbreviation	Structural Formula (at pH 6)
aspartic acid	asp (D)	
glutamic acid	glu (E)	
		Amino acids with a positively charged R group
histidine	his (H)	

Common Name	Abbreviation	Structural Formula (at pH 6)
lysine	lys (K)	
arginine	arg (R)	

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning "sweet"). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



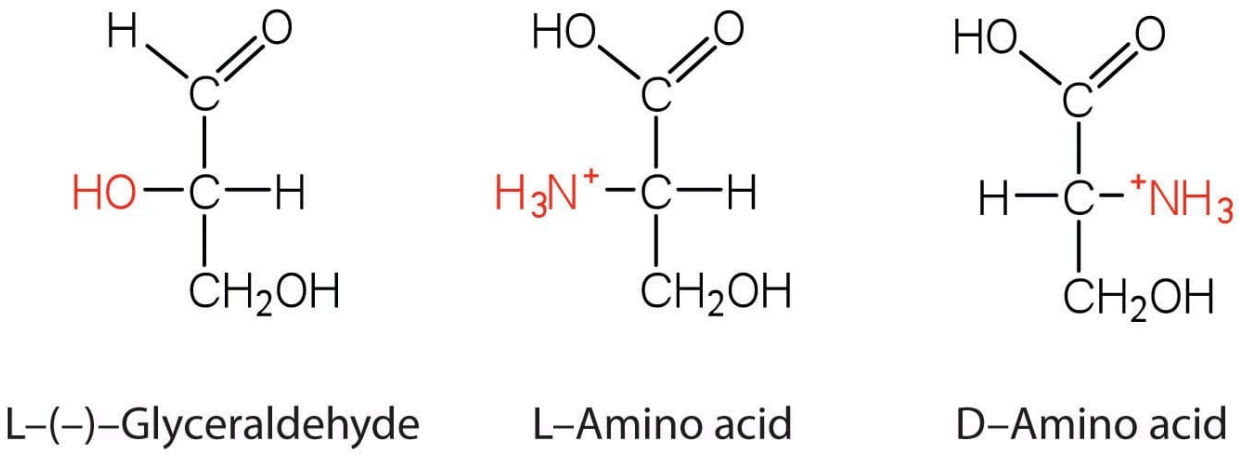
Proline



Hydroxyproline

Configuration

Notice in Table 24.9.1 that glycine is the only amino acid whose α-carbon is *not* chiral. Therefore, with the exception of glycine, the amino acids could theoretically exist in either the D- or the L-enantiomeric form and rotate plane-polarized light. As with sugars, chemists used L-glyceraldehyde as the reference compound for the assignment of absolute configuration to amino acids. Its structure closely resembles an amino acid structure except that in the latter, an amino group takes the place of the OH group on the chiral carbon of the L-glyceraldehyde and a carboxylic acid replaces the aldehyde. Modern stereochemistry assignments using the Cahn-Ingold-Prelog priority rules used ubiquitously in chemistry show that all of the naturally occurring chiral amino acids are S except Cys which is R.



We learned that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of L-amino acids. However, certain bacteria contain D-amino acids in their cell walls, and several antibiotics (e.g., actinomycin D and the gramicidins) contain varying amounts of D-leucine, D-phenylalanine, and D-valine.

Summary

Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure.
- Explain what happens when proteins are denatured.
- Identify how a protein can be denatured.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions.

Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

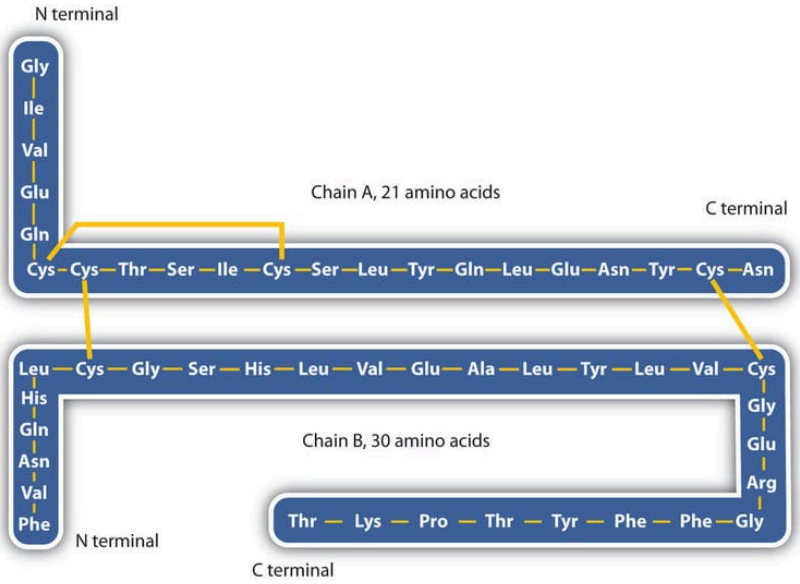


Figure 24.9.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the primary structure, which is the number and sequence of amino acids in a protein's polypeptide chain or chains, beginning with the free amino group and maintained by the peptide bonds connecting each amino acid to the next. The primary structure of insulin, composed of 51 amino acids, is shown in Figure 24.9.1.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term secondary structure refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α-helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure 24.9.2). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

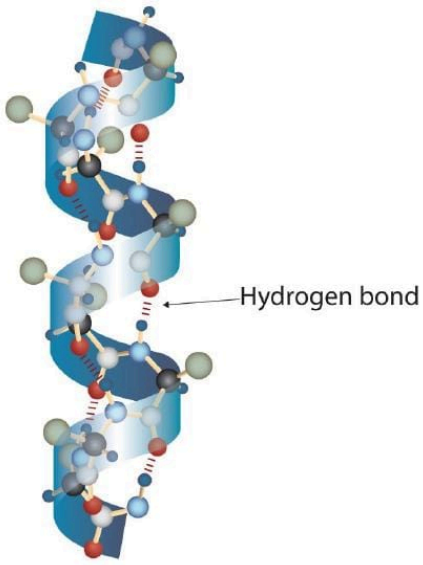


Figure 24.9.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the *β-pleated sheet conformation*, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—and are connected by *interchain* hydrogen bonding (Figure 24.9.3). The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

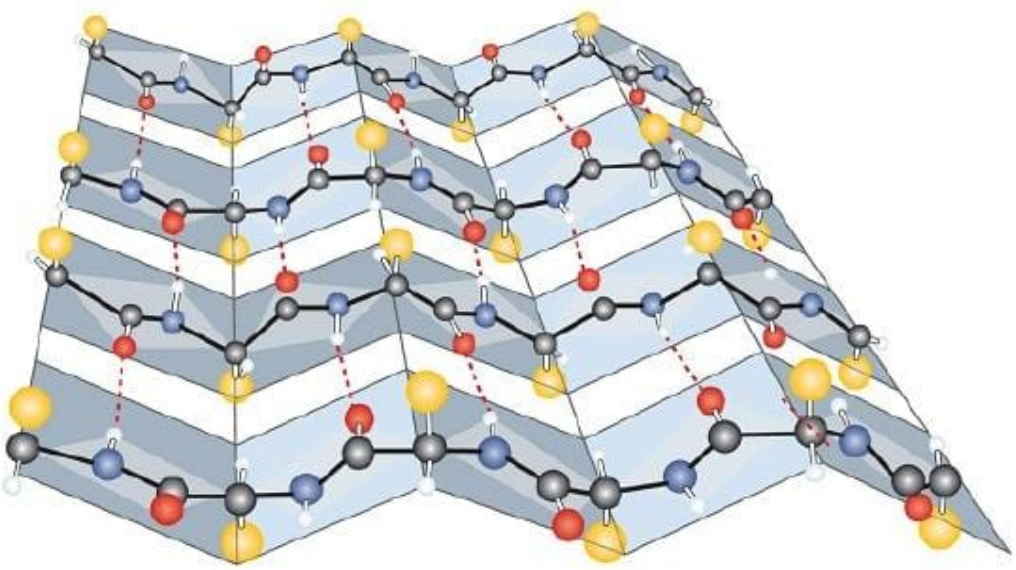


Figure 24.9.3: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure 24.9.4 shows a depiction of the three-dimensional structure of insulin.

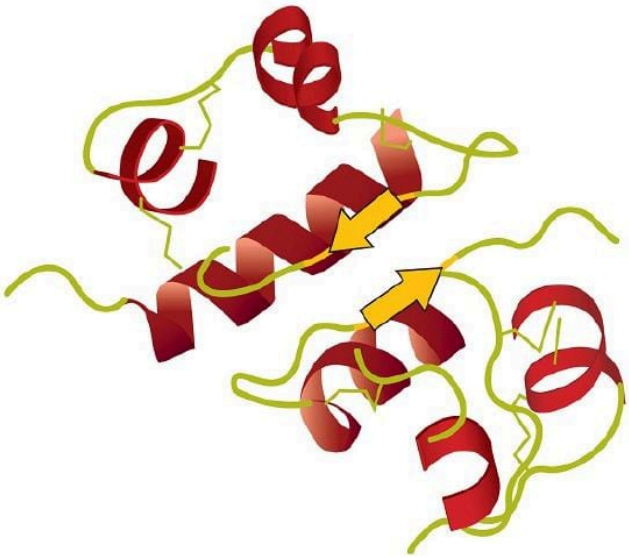
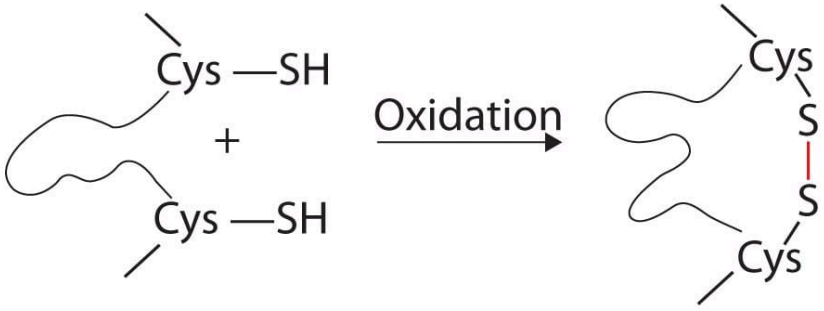


Figure 24.9.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins. You studied several of them previously.

1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure 24.9.5).
2. Hydrogen bonding. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure 24.9.5).
3. Disulfide linkages. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure 24.9.5). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 24.9.1) and have a strong stabilizing effect on the tertiary structure.



4. Dispersion forces. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of Figure 24.9.5). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

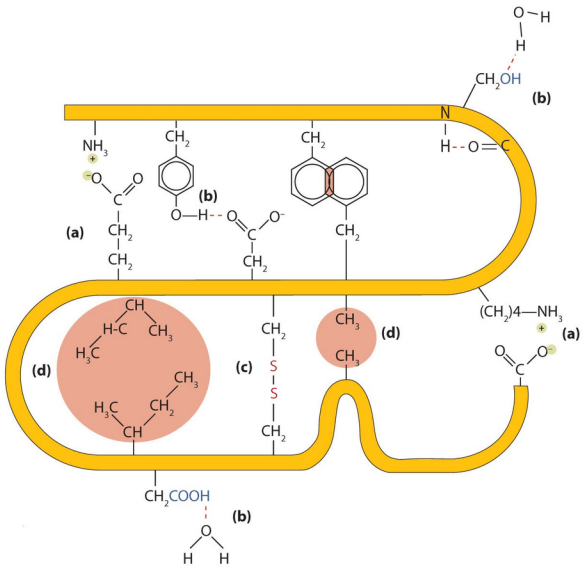


Figure 24.9.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure 24.9.6). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure 24.9.7.

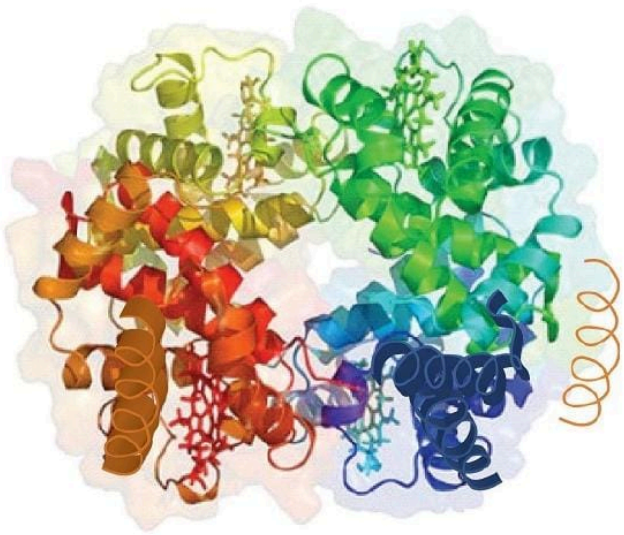


Figure 24.9.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org(opens in new window)) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

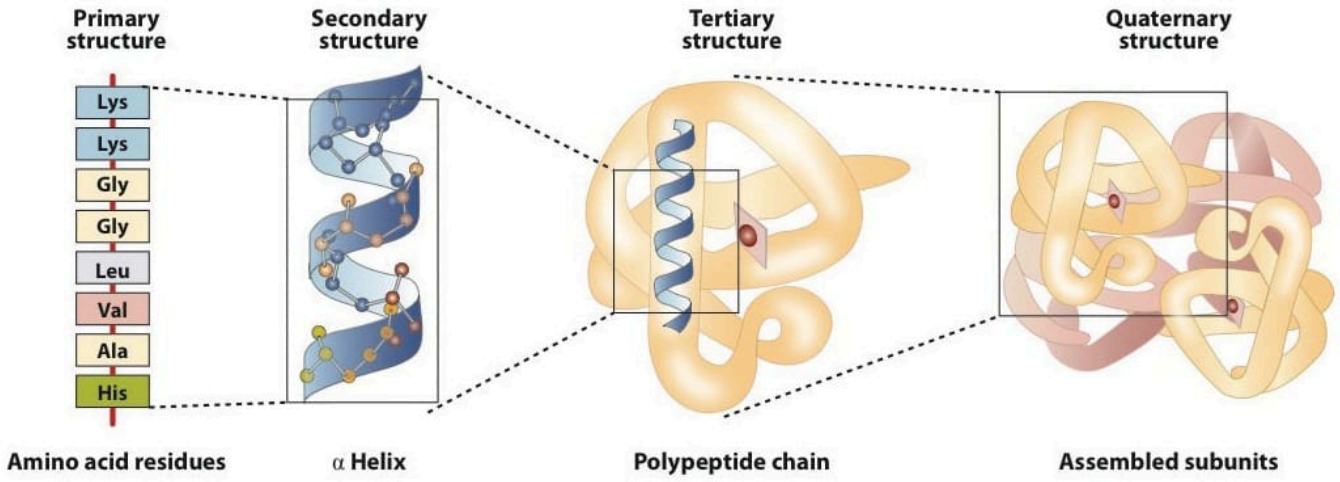


Figure 24.9.7: Levels of Structure in Proteins

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure 24.9.1).

Figure 24.9.1: Protein Denaturation Methods

Method	Effect on Protein Structure
Heat above 50°C or ultraviolet (UV) radiation	Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces.
Use of organic compounds, such as ethyl alcohol	These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein.
Salts of heavy metal ions, such as mercury, silver, and lead	These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages.
Alkaloid reagents, such as tannic acid (used in tanning leather)	These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds.

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity (Figure 24.9.8). Such evidence suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

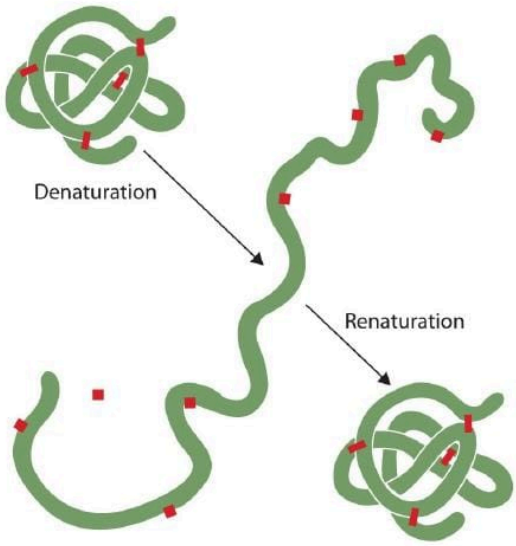


Figure 24.9.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

Summary

Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure. The primary structure consists of the specific amino acid sequence. The resulting peptide chain can form an α-helix or β-pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain. The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces. A wide variety of reagents and conditions can cause a protein to unfold or denature.

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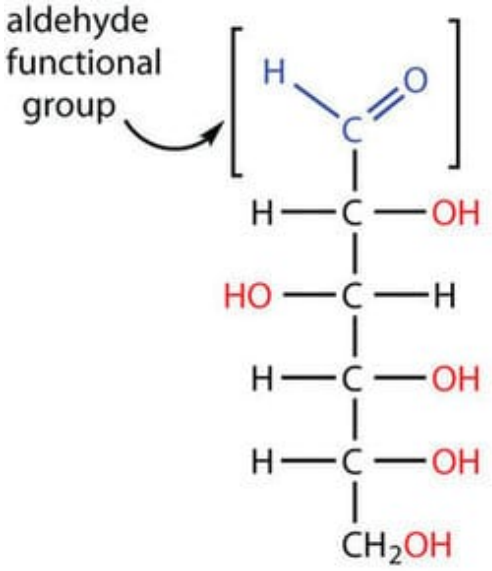
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24.10: Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $C_6H_{12}O_6$, glucose was once thought to be a "carbon hydrate" with the structure $C_6 \cdot 6H_2O$.

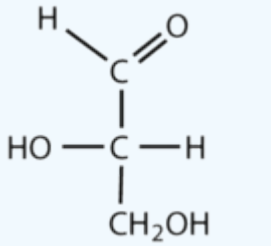


Because glucose has an aldehyde functional group and several –OH (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

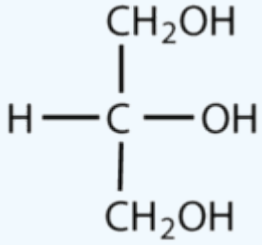
Example 24.10.1

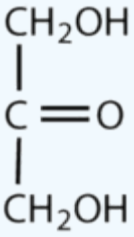
Which compounds would be classified as carbohydrates?

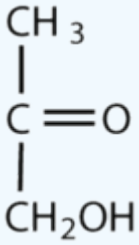
a.



b.



c. 

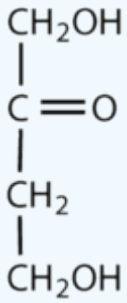
d. 

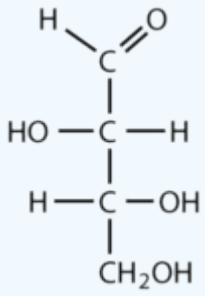
Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.
d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

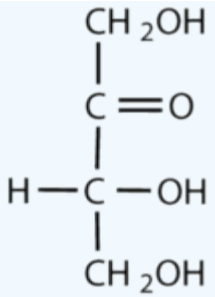
Exercise 24.10.1

Which compounds would be classified as carbohydrates?

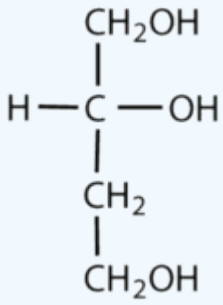
1. 

2. 

3.



4.



Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as photosynthesis:

$$6\,CO_2 + 6\,H_2O + 686\text{ kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{24.10.1}$$

(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called monosaccharides. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. Disaccharide molecules have two monosaccharide units, *trisaccharide* molecules have three units, and so on. Chains with many monosaccharide units joined together are called polysaccharides. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

> Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.

Summary

Carbohydrates are an important group of biological molecules that includes sugars and starches. Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, and polysaccharides contain many monosaccharide units.

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24.11: Nucleic Acids

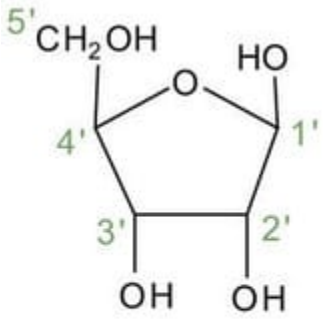
Learning Objectives

- To identify the different molecules that combine to form nucleotides.

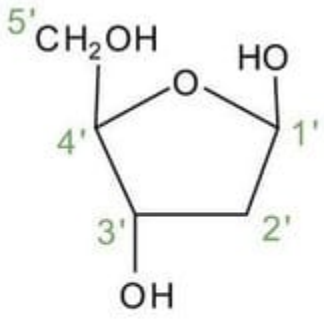
The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3×10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar}$$

If the pentose sugar is ribose, the nucleotide is more specifically referred to as a *ribonucleotide*, and the resulting nucleic acid is ribonucleic acid (RNA). If the sugar is 2-deoxyribose, the nucleotide is a *deoxyribonucleotide*, and the nucleic acid is DNA.



β-Ribose
(found in RNA)



β-2-Deoxyribose
(found in DNA)

The nitrogenous bases found in nucleotides are classified as pyrimidines or purines. Pyrimidines are heterocyclic amines with two nitrogen atoms in a six-member ring and include uracil, thymine, and cytosine. Purines are heterocyclic amines consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms. Adenine and guanine are the major purines found in nucleic acids (Figure 24.11.1).

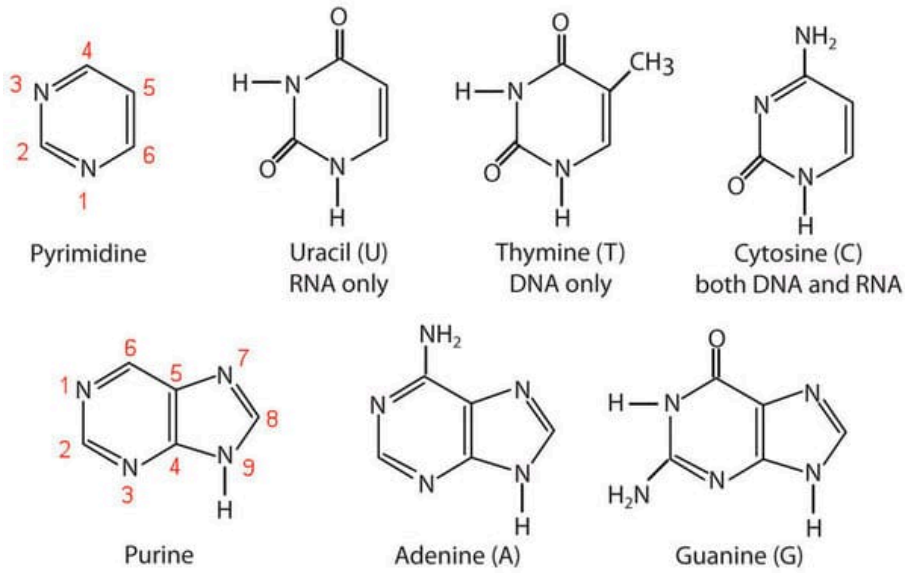


Figure 24.11.1: The Nitrogenous Bases Found in DNA and RNA

The formation of a bond between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table 24.11.1 summarizes the similarities and differences in the composition of nucleotides in DNA and RNA.

> The numbering convention is that primed numbers designate the atoms of the pentose ring, and unprimed numbers designate the atoms of the purine or pyrimidine ring.

Table 24.11.1: Composition of Nucleotides in DNA and RNA

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine
pyrimidine bases	cytosine and thymine	cytosine and uracil
pentose sugar	2-deoxyribose	ribose
inorganic acid	phosphoric acid (H_3PO_4)	H_3PO_4

The names and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure 24.11.2.

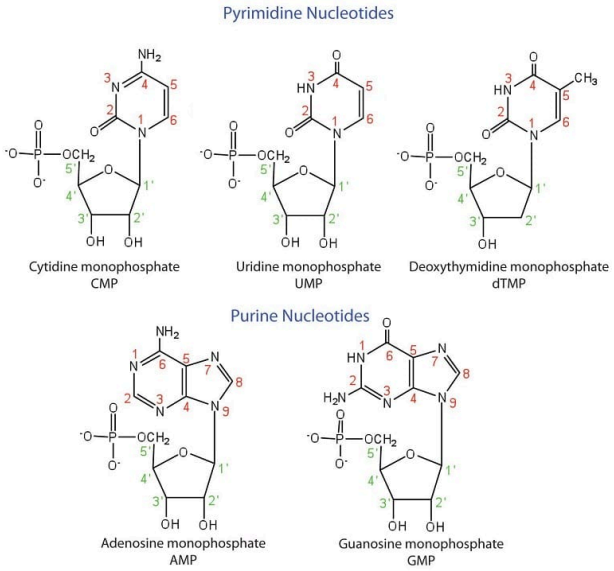


Figure 24.11.2: The Pyrimidine and Purine Nucleotides

Apart from being the monomer units of DNA and RNA, the nucleotides and some of their derivatives have other functions as well. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP), shown in Figure 24.11.3, have a role in cell metabolism. Moreover, a number of coenzymes, including flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide (NAD^+), and coenzyme A, contain adenine nucleotides as structural components.

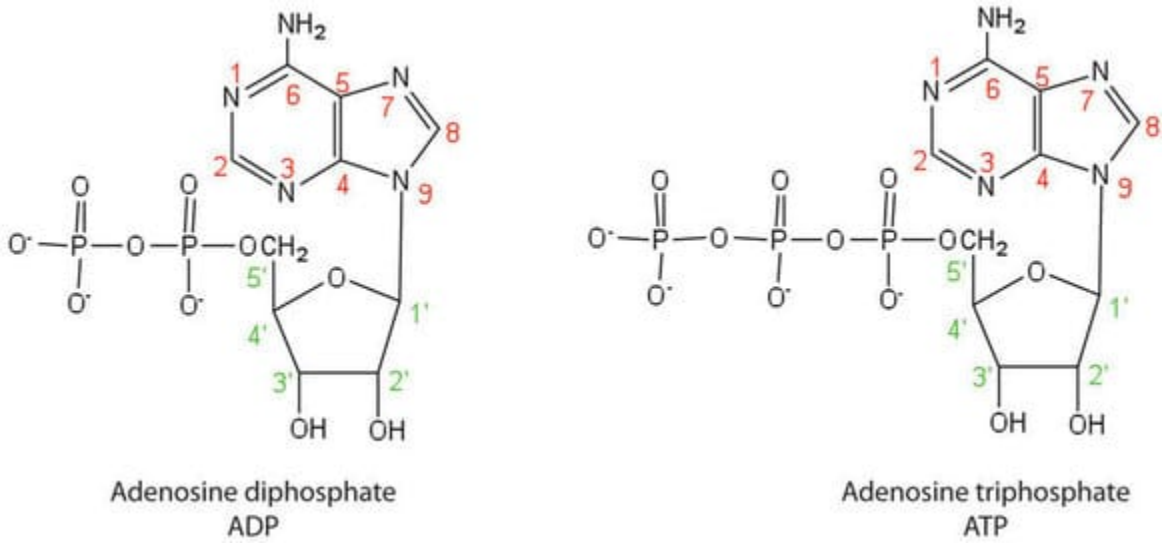


Figure 24.11.3: Structures of Two Important Adenine-Containing Nucleotides

Summary

Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.

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24.E: Organic and Biological Chemistry (Exercises)

25.1: General Characteristics of Organic Molecules

Concept Review Exercises

1. Classify each compound as organic or inorganic.

    a. C_3H_8O
    b. $CaCl_2$
    c. $Cr(NH_3)_3Cl_3$
    d. $C_{30}H_{48}O_3N$

2. Which compound is likely organic and which is likely inorganic?

    a. a flammable compound that boils at 80°C and is insoluble in water
    b. a compound that does not burn, melts at 630°C, and is soluble in water

Answers

1. a. organic
    b. inorganic
    c. inorganic
    d. organic
2. a. organic
    b. inorganic

Exercises

1. Classify each compound as organic or inorganic.

    a. C_6H_{10}
    b. $CoCl_2$
    c. $C_{12}H_{22}O_{11}$

2. Classify each compound as organic or inorganic.

    a. CH_3NH_2
    b. $NaNH_2$
    c. $Cu(NH_3)_6Cl_2$

3. Which member of each pair has a higher melting point?

    a. CH_3OH and NaOH
    b. CH_3Cl and KCl

4. Which member of each pair has a higher melting point?

    a. C_2H_6 and $CoCl_2$
    b. CH_4 and LiH

Answers

1. a. organic
   b. inorganic
   c. organic

3. a. NaOH
   b. KCl

25.2: Introduction to Hydrocarbons

25.3: Alkanes

25.4: Unsaturated Hydrocarbons

25.5: Functional Groups

Concept Review Exercises

1. What is the functional group of an alkene? An alkyne?
2. Does $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ have a functional group? Explain.

Answers

1. carbon-to-carbon double bond; carbon-to-carbon triple bond
2. No; it has nothing but carbon and hydrogen atoms and all single bonds.

Exercises

1. What is the functional group of 1-butanol ($CH_3CH_2CH_2CH_2OH$)?
2. What is the functional group of butyl bromide, $CH_3CH_2CH_2CH_2Br$?

Answer

1. OH

25.6: Compounds with a Caronyl Group

25.7: Chirality in Organic Chemistry

25.8: Introduction to Biochemistry

25.9: Proteins

25.10: Carbohydrates

25.11: Nucleic Acids

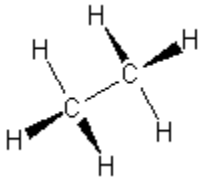
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24.S: Organic and Biological Chemistry (Summary)

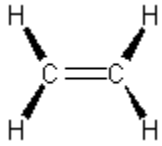
- **organic chemistry** – the study of carbon compounds
- **biochemistry** – the study of the chemistry of living species

25.2: Introduction to Hydrocarbons

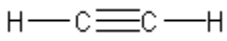
- made of only hydrogen and carbon
- 4 types: alkanes, alkenes, alkynes, and aromatic hydrocarbons
- **alkanes** – only single bonds
- also called saturated hydrocarbons



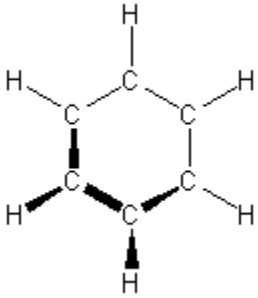
- have the largest amount of hydrogen atoms bonded to a single carbon atom
-



- **alkenes** (olefins) – have double carbon bonds
- ◦ **alkynes** – triple carbon bonds



- ◦ **aromatic hydrocarbons** – carbon atoms connected in a planar ring structure, joined by s and p bonds between carbon atoms



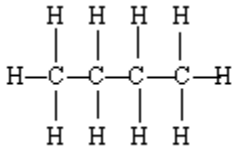
- ◦ **alkenes, alkynes and aromatic hydrocarbons** – unsaturated hydrocarbons
  ◦ less volatile with increasing molar mass
  ◦ very low molecular weight = gas at room temperature
  ◦ moderate molecular weight = liquid
  ◦ high molecular weight = solid

25.3: Alkanes

- methane major part of natural gas
- used in home heating, gas stoves, hot-water heaters
- propane major part of bottled gas
- used for home heating, cooking
- butane – used in disposable lighters, fuel canisters
- alkanes with 5-12 carbon atoms are found in gasoline
- formla for alkanes is called *condensed structural formulas*

Condensed Structural Formulas

Molecular Formula	Condensed Structural Formula	Name	Boiling point (°C)
CH_4	CH_4	Methane	-161
C_2H_6	$CH_3\ CH_3$	Ethane	-89
C_3H_8	$CH_3\ CH_2\ CH_3$	Propane	-44
C_4H_{10}	$CH_3\ CH_2\ CH_2\ CH_3$	Butane	-0.5
C_5H_{12}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_3$	Pentane	36
C_6H_{14}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$	Hexane	68
C_7H_{16}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$	Heptane	98
C_8H_{18}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$	Octane	125
C_9H_{20}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$	Nonane	151
$C_{10}H_{22}$	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$	Decane	174



Lewis Structure

1. **Structures of Alkanes**

- ◦ tetrahedral geometry
  ◦ carbon-carbon single bond rotates easily at room temperature
  ◦ long chains tend to change shape

1. **Structural Isomers**

- ◦ straight-chained hydrocarbons – carbons atoms that are joined in a continuous chain
  ◦ branched-chain hydrocarbons – hydrocarbons with branched chains, 4 or more carbon atoms
  ◦ **structural isomers** – compounds with the same molecular formula but different bonding arrangements

1. **Nomenclature of Alkanes**

- ◦ **1)** Find the longest continuous chain of carbon atoms, and use the name of this chain as the base name of the compound.
  ◦ **2)** Number the carbon atoms in the longest chain, beginning with the end of the chain that is nearest to a substituent
  ◦ **3)** Name and give the location of each substituent group
  ◦ **4)** When two or more substituents are present list them in alphabetical order

1. **Cycloalkanes**

- ◦ alkanes that form rings or cycles
  ◦ carbon rings with fewer than five carbon atoms are strained
  ◦ more reactive

1. **Reactions of Alkanes**

- ◦ at room temperature alkanes do not react with acids, bases, or strong oxidizing agents
  ◦ important for it's combustion in air; bases for fuels

25.4: Unsaturated Hydrocarbons

- **Alkenes**
- ◦ double carbon bonds
  ◦ ethene or ethylene simplest alkene\
  ◦ nomenclature of alkenes come from the name of the corresponding alkane
  ◦ the –ane ending is changed to –ene
  ◦ **geometrical isomers** – compounds that have the same molecular formula and the same groups bonded to one another but differ in the spatial arrangement of these groups
  ◦ geometrical isomers have distinct physical properties and differ in chemical behavior
  ◦ the double carbon bond is resistant to twisting
  ◦ rotation about a double bond is a key process in the chemistry of vision

1. **Alkynes**

- ◦ one or more triple bonds
  ◦ simplest alkyne is acetylene
  ◦ highly reactive
  ◦ named by changing the alkane ending (-ane) to –yne

1. **Addition Reactions of Alkenes and Alkynes**

- ◦ **addition reactions** – a reactant is added to the two atoms that form the multiple bond
  ◦ **hyrogenation** – reaction between al alkene and H_2

1. **Aromatic Hydrocarbons**

- ◦ simplest is benzene
  ◦ stability comes from the stabilization of the p electrons through delocalization in the p orbitals
  ◦ represented by a hexagon with an inscribed circle
  ◦ **substitution reactions** – one atom of a molecule is removed and replaced by another atom or group of atoms

25.5: Functional Groups

functional group – site of reactivity in an organic molecule; controls how the molecule behaves or functions

- chemistry of an organic molecule is determined by the functional groups it contains

1. **Alcohols (R-OH)**

- **alcohols** – hydrocarbon derivatives in which one ore more hydrogens of a parent hydrocarbon have been replaced by a hydroxyle or alcohol functional group

1. **Ethers (R-O-R')**

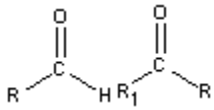
- ◦ **ethers** – two hyrocarbon groups are bonded to one oxygen
  ◦ formed from two molecules of alcohol by splitting out a molecule of water

- **condensation reaction** – reaction where water is split out from two substances
- used in solvents

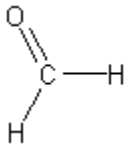
25.6: Compounds with a Carbonyl Group

- carbon oxygen double bonds

1. **Aldehydes and Ketones**

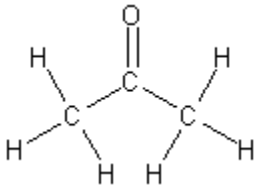


- carbonyl group in aldehydes has at least one attached hydrogen atom



formaldehyde

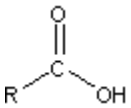
- carbonyl group in ketones occurs at the interior of a carbon chain



Acetone

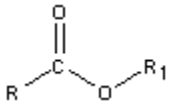
- prepared by oxidizing alcohols

1. **Carboxylic Acids**



- carboxylic acids contain carboxyl functional group (COOH)
- important for manufacturing of polymers
- produced by oxidation in which the OH group is attached to the CH_2

1. **Esters**



- carboxylic acids that undergo condensation with alcohols
- have pleasant odors
- saponification – hydrolysis of an ester in a base

1. **Amines and Amides**

- **amines** – organic bases; general formula R_3N
- **amides** – anines containing a hydrogen bonded to nitrogen that undergoes condensation

25.8: Introduction to Biochemistry

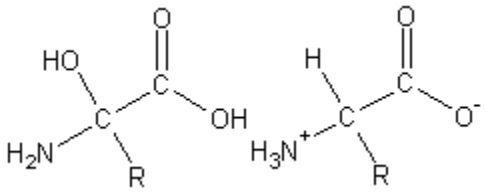
- **biosphere** – part of the earth where living organisms are formed and living
- includes influences on life of the atmosphere, natural waters, solid earth
- living organisms require a large amount of energy
- **biopolymers** – three categories: proteins, polysaccharides (carbohydrates), and nucleic acids

25.9: Proteins

- macromolecular substances
- 50% body's dry weight is proteins
- composed of amino acids

1. **Amino Acids**

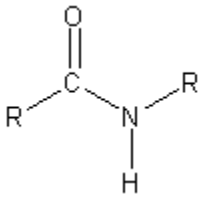
- differ in the R group
- building block of all proteins - a -amino acid
- general form:



- **chiral** - any molecule containing a carbon with four different attached groups
- **enantiomers** – mirror-image of chiral
- enantiomers and chiral have the same physical properties
- differ in chemical reactivity toward other chiral molecules

1. **Polypeptides and Proteins**

- **peptide bond** – condesation reaction between the carboxyl group of one amino acid and the amino group of another amino acid



- **polypeptides** – large number of amino acids that are linked together by peptide bonds
- proteins are polypeptide molecules
- weighs from 6000 to over 50 million amu

1. **Protein Structure**

- **primary structure** – arrangement of amino acids along a protein chain
- makes the protein unique

- **secondary structure** – the way segments of the protein chain are oriented in a regular pattern
- **α -helix** – most important and common secondary structure arrangement
- first propoesed by Linus Pauling and R. B. Corey
- **tertiary structure** – overal shape of a protein
- **globular protein** – a protein that folds into a compact spherical shape
- soluble in water, mobile within cells
- **enzymes** – large protein molecules that serve as catalysts

25.10: Carbohydrates

- written as $C_x(H_2O)_y$
- glucose the most abundant carbohydrate $C_6H_{12}O_6$
- not really hydrates of carbon but polyhydroxly aldehydes and ketones

1. **Disaccharides**

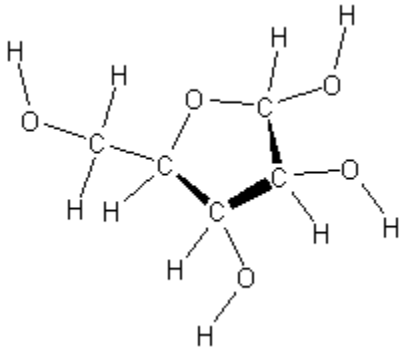
- **monosaccharides** – simple sugars that can't be broken into smaller molecules by hydrolysis with aqueous acids
- **disaccharide** – two linked monosaccharides
- two common disaccharides: sucrose, lactose

1. **Polysaccharides**

- made of several monosaccharide units
- **starch** – group of polysaccharides
- food storage in plant seeds and tuers
- **glycogen** – starchlike substance synthesized in the body
- 5000 to more than 5 million amu
- energy bank in the body; muscles and liver
- cellulose – major strructural unit of plants
- straight chains of glucose units
- more than 500,000 amu

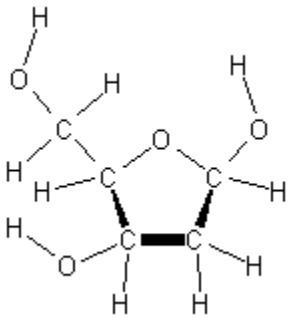
25.11: Nucleic Acids

- **nucleic acids** – biopolymers that are chemical carriers of an organisn't genetic information
- **deoxyribonucleic acids (DNA)** – huge molecules with molar weights of 6-16million amu
- **ribonucleic acids (RNA)** – smaller molecules with molecular weights of 20,000 to 40,000 amu
- DNA found inside the nucleus of a cell, RNA found outside nucleus in the cytoplasm
- DNA stores the genetic information of the cell and controls the production of proteins
- RNA carries information from the DNA out of the nucleus
- Monomers of nucleic acids (nucleotides) have three parts:
  - A phosphoric acid molecule, H_3PO_4
  - A five-carbon sugar



ribose

- A nitrogen-containing organic base



deoxyribose

- ◦ deoxyribose has one less oxygen atom at carbon 2 than ribose
  ◦ nucleic acids are polynucleotides
  ◦ DNA molecules made of two DNA chains that form a double helix

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GLOSSARY

A

accuracy | how closely a measurement aligns with a correct value

acid anhydride | compound that reacts with water to form an acid or acidic solution

acid ionization | reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

acid ionization constant (K_a) | equilibrium constant for the ionization of a weak acid

acid-base indicator | organic acid or base whose color changes depending on the pH of the solution it is in

acidic | describes a solution in which $[\mathrm{H_3O^+}] > [\mathrm{OH^-}]$

actinide | inner transition metal in the bottom of the bottom two rows of the periodic table

actinide series | (also, actinoid series) actinium and the elements in the second row or the *f*-block, atomic numbers 89–103

activated complex | (also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

activation energy (E_a) | energy necessary in order for a reaction to take place

active electrode | electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

actual yield | amount of product formed in a reaction

addition reaction | reaction in which a double carbon-carbon bond forms a single carbon-carbon bond by the addition of a reactant. Typical reaction for an alkene.

adhesive force | force of attraction between molecules of different chemical identities

alcohol | organic compound with a hydroxyl group (–OH) bonded to a carbon atom

alkali metal | element in group 1

alkaline earth metal | element in group 2

alkaline earth metal | any of the metals (beryllium, magnesium, calcium, strontium, barium, and radium) occupying group 2 of the periodic table; they are reactive, divalent metals that form basic oxides

alkane | molecule consisting of only carbon and hydrogen atoms connected by single (σ) bonds

alkene | molecule consisting of carbon and hydrogen containing at least one carbon-carbon double bond

alkyl group | substituent, consisting of an alkane missing one hydrogen atom, attached to a larger structure

alkyne | molecule consisting of carbon and hydrogen containing at least one carbon-carbon triple bond

allotropes | two or more forms of the same element, in the same physical state, with different chemical structures

alloy | solid mixture of a metallic element and one or more additional elements

alpha (α) decay | loss of an alpha particle during radioactive decay

alpha particle | (α or $^4_2\mathrm{He}$ or $^4_2\alpha$) high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

alpha particle (α particle) | positively charged particle consisting of two protons and two neutrons

amide | organic molecule that features a nitrogen atom connected to the carbon atom in a carbonyl group

amine | organic molecule in which a nitrogen atom is bonded to one or more alkyl group

amorphous | solid material such as a glass that does not have a regular repeating component to its three-dimensional structure; a solid but not a crystal

amorphous solid | (also, noncrystalline solid) solid in which the particles lack an ordered internal structure

amphiphilic | molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

amphiprotic | species that may either gain or lose a proton in a reaction

amphoteric | species that can act as either an acid or a base

amplitude | extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

analyte | chemical species of interest

angular momentum quantum number (l) | quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

anion | negatively charged atom or molecule (contains more electrons than protons)

anode | electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

antimatter | particles with the same mass but opposite properties (such as charge) of ordinary particles

aqueous solution | solution for which water is the solvent

aromatic hydrocarbon | cyclic molecule consisting of carbon and hydrogen with delocalized alternating carbon-carbon single and double bonds, resulting in enhanced stability

Arrhenius equation | mathematical relationship between the rate constant and the activation energy of a reaction

atmosphere (atm) | unit of pressure; 1 atm = 101,325 Pa

atom | smallest particle of an element that can enter into a chemical combination

atomic mass | average mass of atoms of an element, expressed in amu

atomic mass unit (amu) | (also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a ^{12}C atom

atomic number (Z) | number of protons in the nucleus of an atom

atomic orbital | mathematical function that describes the behavior of an electron in an atom (also called the wavefunction), it can be used to find the probability of locating an electron in a specific region around the nucleus, as well as other dynamical variables

Aufbau principle | procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

autoionization | reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

average rate | rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

Avogadro's number (N_A) | experimentally determined value of the number of entities comprising 1 mole of substance, equal to 6.022×10^{23} mol^{-1}

axial position | location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

B

balanced equation | chemical equation with equal numbers of atoms for each element in the reactant and product

band of stability | (also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

bar | (bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer | device used to measure atmospheric pressure

base anhydride | metal oxide that behaves as a base towards acids

base ionization | reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

base ionization constant (K_b) | equilibrium constant for the ionization of a weak base

basic | describes a solution in which $[H_3O^+] < [OH^-]$

becquerel (Bq) | SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s

beta (β) decay | breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

beta particle | (β or $_{-1}^{0}e$ or $_{-1}^{0}\beta$) high-energy electron

bicarbonate anion | salt of the hydrogen carbonate ion, HCO_3^-

bidentate ligand | ligand that coordinates to one central metal through coordinate bonds from two different atoms

binary acid | compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound | compound containing two different elements.

binding energy per nucleon | total binding energy for the nucleus divided by the number of nucleons in the nucleus

bismuth | heaviest member of group 15; a less reactive metal than other representative metals

blackbody | idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

body-centered cubic (BCC) solid | crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

body-centered cubic unit cell | simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

Bohr's model of the hydrogen atom | structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius; the orbiting electron does not normally emit electromagnetic radiation, but does so when changing from one orbit to another.

boiling point | temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

boiling point elevation | elevation of the boiling point of a liquid by addition of a solute

boiling point elevation constant | the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

bomb calorimeter | device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

bond angle | angle between any two covalent bonds that share a common atom

bond dipole moment | separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

bond distance | (also, bond length) distance between the nuclei of two bonded atoms

bond energy | (also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

bond length | distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

borate | compound containing boron-oxygen bonds, typically with clusters or chains as a part of the chemical structure

Born-Haber cycle | thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

Bragg equation | equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

Brønsted-Lowry acid | proton donor

Brønsted-Lowry base | proton acceptor

buffer | mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

buffer capacity | amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buret | device used for the precise delivery of variable liquid volumes, such as in a titration analysis

C

calorie (cal) | unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

calorimeter | device used to measure the amount of heat absorbed or released in a chemical or physical process

calorimetry | process of measuring the amount of heat involved in a chemical or physical process

capillary action | flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

carbonate | salt of the anion CO_3^{2-}; often formed by the reaction of carbon dioxide with bases

catalyst | substance that increases the rate of a reaction without itself being consumed by the reaction

cathode | electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

cathodic protection | method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

cation | positively charged atom or molecule (contains fewer electrons than protons)

cell notation | shorthand way to represent the reactions in an electrochemical cell

cell potential | difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

Celsius (°C) | unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

central metal | ion or atom to which one or more ligands is attached through coordinate covalent bonds

chain reaction | repeated fission caused when the neutrons released in fission bombard other atoms

chalcogen | element in group 16

chelate | complex formed from a polydentate ligand attached to a central metal

chelating ligand | ligand that attaches to a central metal ion by bonds from two or more donor atoms

chemical change | change producing a different kind of matter from the original kind of matter

chemical equation | symbolic representation of a chemical reaction

chemical property | behavior that is related to the change of one kind of matter into another kind of matter

chemical reduction | method of preparing a representative metal using a reducing agent

chemical symbol | one-, two-, or three-letter abbreviation used to represent an element or its atoms

chemical thermodynamics | area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

chemistry | study of the composition, properties, and interactions of matter

chemotherapy | similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

chlor-alkali process | electrolysis process for the synthesis of chlorine and sodium hydroxide

circuit | path taken by a current as it flows because of an electrical potential difference

***cis* configuration** | configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

Clausius-Clapeyron equation | mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

coefficient | number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

cohesive force | force of attraction between identical molecules

colligative property | property of a solution that depends only on the concentration of a solute species

collision theory | model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

colloid | (also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

color-change interval | range in pH over which the color change of an indicator takes place

combustion analysis | gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

common ion effect | effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

complete ionic equation | chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

compound | pure substance that can be decomposed into two or more elements

compressibility factor (Z) | ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

concentrated | qualitative term for a solution containing solute at a relatively high concentration

concentration | quantitative measure of the relative amounts of solute and solvent present in a solution

concentration cell | galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

condensation | change from a gaseous to a liquid state

conjugate acid | substance formed when a base gains a proton

conjugate base | substance formed when an acid loses a proton

containment system | (also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

continuous spectrum | electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

control rod | material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

coordination compound | stable compound in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons

coordination compound | substance consisting of atoms, molecules, or ions attached to a central atom through Lewis acid-base interactions

coordination number | number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

coordination number | number of coordinate covalent bonds to the central metal atom in a complex or the number of closest contacts to an atom in a crystalline form

coordination sphere | central metal atom or ion plus the attached ligands of a complex

core electron | electron in an atom that occupies the orbitals of the inner shells

corrosion | degradation of metal through an electrochemical process

covalent bond | attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

covalent bond | bond formed when electrons are shared between atoms

covalent compound | (also, molecular compound) composed of molecules formed by atoms of two or more different elements

covalent network solid | solid whose particles are held together by covalent bonds

covalent radius | one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

crenation | process whereby biological cells become shriveled due to loss of water by osmosis

critical mass | amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

critical point | temperature and pressure above which a gas cannot be condensed into a liquid

crystal field splitting (Δ_{oct}) | difference in energy between the t_{2g} and e_g sets or t and e sets of orbitals

crystal field theory | model that explains the energies of the orbitals in transition metals in terms of electrostatic interactions with the ligands but does not include metal ligand bonding

crystalline solid | solid in which the particles are arranged in a definite repeating pattern

cubic centimeter (cm^3 or cc) | volume of a cube with an edge length of exactly 1 cm

cubic closest packing (CCP) | crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

cubic meter (m^3) | SI unit of volume

curie (Ci) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

current | flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes $\left(1\ \text{A} = 1\ \frac{\text{C}}{\text{s}}\right)$

D

***d* orbital** | region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$. An electron in this orbital is called a *d* electron

***d*-block element** | one of the elements in groups 3–11 with valence electrons in *d* orbitals

Dalton (Da) | alternative unit equivalent to the atomic mass unit

Dalton's atomic theory | set of postulates that established the fundamental properties of atoms

daughter nuclide | nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

density | ratio of mass to volume for a substance or object

deposition | change from a gaseous state directly to a solid state

diffraction | redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions

dilute | qualitative term for a solution containing solute at a relatively low concentration

dilution | process of adding solvent to a solution in order to lower the concentration of solutes

dimensional analysis | (also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

dipole moment | property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

dipole-dipole attraction | intermolecular attraction between two permanent dipoles

diprotic acid | acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base | base capable of accepting two protons. The protons are accepted in two steps

dispersed phase | substance present as relatively large solid or liquid particles in a colloid

dispersion force | (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

dispersion medium | solid, liquid, or gas in which colloidal particles are dispersed

disproportionation reaction | chemical reaction where a single reactant is simultaneously reduced and oxidized; it is both the reducing agent and the oxidizing agent

dissociation | physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

dissolved | describes the process by which solute components are dispersed in a solvent

donor atom | atom in a ligand with a lone pair of electrons that forms a coordinate covalent bond to a central metal

double bond | covalent bond in which two pairs of electrons are shared between two atoms

Downs cell | electrochemical cell used for the commercial preparation of metallic sodium (and chlorine) from molten sodium chloride

dynamic equilibrium | state of a system in which reciprocal processes are occurring at equal rates

E

effective nuclear charge | charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

e_g orbitals | set of two *d* orbitals that are oriented on the Cartesian axes for coordination complexes; in octahedral complexes, they are higher in energy than the t_{2g} orbitals

electrical potential | energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt $\left(1\ \text{V} = 1\ \frac{\text{J}}{\text{C}}\right)$

electrical work (w_{ele}) | negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

electrolyte | substance that produces ions when dissolved in water

electromagnetic radiation | energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum | range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

electron | negatively charged, subatomic particle of relatively low mass located outside the nucleus

electron affinity | energy required to add an electron to a gaseous atom to form an anion

electron capture | combination of a core electron with a proton to yield a neutron within the nucleus

electron configuration | electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

electron density | a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

electron volt (eV) | measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

electron-pair geometry | arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

electronegativity | tendency of an atom to attract electrons in a bond to itself

element | substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

empirical formula | formula showing the composition of a compound given as the simplest whole-number ratio of atoms

empirical formula mass | sum of average atomic masses for all atoms represented in an empirical formula

emulsifying agent | amphiphilic substance used to stabilize the particles of some emulsions

emulsion | colloid formed from immiscible liquids

end point | measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see *equivalence point*)

endothermic process | chemical reaction or physical change that absorbs heat

energy | capacity to supply heat or do work

enthalpy (*H*) | sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change (Δ*H*) | heat released or absorbed by a system under constant pressure during a chemical or physical process

entropy (S) | state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

equatorial position | one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

equilibrium | in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

equilibrium constant (*K*) | value of the reaction quotient for a system at equilibrium

equivalence point | volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

ether | organic compound with an oxygen atom that is bonded to two carbon atoms

exact number | number derived by counting or by definition

excess reactant | reactant present in an amount greater than required by the reaction stoichiometry

excited state | state having an energy greater than the ground-state energy

exothermic process | chemical reaction or physical change that releases heat

expansion work (pressure-volume work) | work done as a system expands or contracts against external pressure

extensive property | property of a substance that depends on the amount of the substance

external beam radiation therapy | radiation delivered by a machine outside the body

F

***f* orbital** | multilobed region of space with high electron density, describes orbitals with $l = 3$. An electron in this orbital is called an *f* electron

***f*-block element** | (also, inner transition element) one of the elements with atomic numbers 58–71 or 90–103 that have valence electrons in *f* orbitals; they are frequently shown offset below the periodic table

face-centered cubic (FCC) solid | crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

face-centered cubic unit cell | simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

Fahrenheit | unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

Faraday's constant (F) | charge on 1 mol of electrons; $F = 96{,}485$ C/mol e^-

first law of thermodynamics | internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

first transition series | transition elements in the fourth period of the periodic table (first row of the *d*-block), atomic numbers 21–29

fissile (or fissionable) | when a material is capable of sustaining a nuclear fission reaction

fission | splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

formal charge | charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

formula mass | sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

fourth transition series | transition elements in the seventh period of the periodic table (fourth row of the *d*-block), atomic numbers 89 and 104–111

Frasch process | important in the mining of free sulfur from enormous underground deposits

free radical | molecule that contains an odd number of electrons

freezing | change from a liquid state to a solid state

freezing point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

freezing point depression | lowering of the freezing point of a liquid by addition of a solute

freezing point depression constant | (also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to

solute molality

frequency (ν) | number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

frequency factor (A) | proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

functional group | part of an organic molecule that imparts a specific chemical reactivity to the molecule

fundamental unit of charge | (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C

fusion | combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

fusion reactor | nuclear reactor in which fusion reactions of light nuclei are controlled

G

galvanic cell | electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

galvanized iron | method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

gamma (γ) emission | decay of an excited-state nuclide accompanied by emission of a gamma ray

gamma ray | (γ or ${}^{0}_{0}\gamma$) short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

gas | state in which matter has neither definite volume nor shape

Geiger counter | instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

gel | colloidal dispersion of a liquid in a solid

geometric isomers | isomers that differ in the way in which atoms are oriented in space relative to each other, leading to different physical and chemical properties

Gibbs free energy change (G) | thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in G

gravimetric analysis | quantitative chemical analysis method involving the separation of an analyte from a sample by a physical or chemical process and subsequent mass measurements of the analyte, reaction product, and/or sample

gray (Gy) | SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

ground state | state in which the electrons in an atom, ion, or molecule have the lowest energy possible

group | vertical column of the periodic table

H

Haber process | main industrial process used to produce ammonia from nitrogen and hydrogen; involves the use of an iron catalyst and elevated temperatures and pressures

half-life ($t_{1/2}$) | time required for half of the atoms in a radioactive sample to decay

half-life of a reaction ($t_{1/2}$) | time required for half of a given amount of reactant to be consumed

half-reaction method | method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation "half" and reduction "half," balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

halide | compound containing an anion of a group 17 element in the 1– oxidation state (fluoride, F^-; chloride, Cl^-; bromide, Br^-; and iodide, I^-)

Hall–Héroult cell | electrolysis apparatus used to isolate pure aluminum metal from a solution of alumina in molten cryolite

halogen | element in group 17

heat (q) | transfer of thermal energy between two bodies

heat capacity (C) | extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

Heisenberg uncertainty principle | rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time. The uncertainty principle is a consequence of quantum particles exhibiting wave–particle duality

hemolysis | rupture of red blood cells due to the accumulation of excess water by osmosis

Henderson-Hasselbalch equation | equation used to calculate the pH of buffer solutions

Henry's law | law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

hertz (Hz) | the unit of frequency, which is the number of cycles per second, s^{-1}

Hess's law | if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

heterogeneous catalyst | catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

heterogeneous equilibria | equilibria between reactants and products in different phases

heterogeneous mixture | combination of substances with a composition that varies from point to point

hexagonal closest packing (HCP) | crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

high-spin complex | complex in which the electrons maximize the total electron spin by singly populating all of the orbitals before pairing two electrons into the lower-energy orbitals

hole | (also, interstice) space between atoms within a crystal

homogeneous catalyst | catalyst present in the same phase as the reactants

homogeneous equilibria | equilibria within a single phase

homogeneous mixture | (also, solution) combination of substances with a composition that is uniform throughout

Hund's rule | every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

hydrocarbon | compound composed only of hydrogen and carbon; the major component of fossil fuels

hydrogen bonding | occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

hydrogen carbonate | salt of carbonic acid, H_2CO_3 (containing the anion HCO_3^-) in which one hydrogen atom has been replaced; an acid carbonate; also known as *bicarbonate ion*

hydrogen halide | binary compound formed between hydrogen and the halogens: HF, HCl, HBr, and HI

hydrogen sulfate | HSO_4^- ion

hydrogen sulfite | HSO_3^- ion

hydrogenation | addition of hydrogen (H_2) to reduce a compound

hydrometallurgy | process in which a metal is separated from a mixture by first converting it into soluble ions, extracting the ions, and then reducing the ions to precipitate the pure metal

hydrostatic pressure | pressure exerted by a fluid due to gravity

hydroxide | compound of a metal with the hydroxide ion OH^- or the group –OH

hypertonic | of greater osmotic pressure

hypervalent molecule | molecule containing at least one main group element that has more than eight electrons in its valence shell

hypothesis | tentative explanation of observations that acts as a guide for gathering and checking information

hypotonic | of less osmotic pressure

I

ideal solution | solution that forms with no accompanying energy change

immiscible | of negligible mutual solubility; typically refers to liquid substances

indicator | substance added to the sample in a titration analysis to permit visual detection of the end point

induced dipole | temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

inert electrode | electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

inert gas | (also, noble gas) element in group 18

inert pair effect | tendency of heavy atoms to form ions in which their valence s electrons are not lost

initial rate | instantaneous rate of a chemical reaction at t = 0 s (immediately after the reaction has begun)

inner transition metal | (also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

instantaneous dipole | temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

instantaneous rate | rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

integrated rate law | equation that relates the concentration of a reactant to elapsed time of reaction

intensity | property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

intensive property | property of a substance that is independent of the amount of the substance

interference pattern | pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

interhalogen | compound formed from two or more different halogens

intermolecular force | noncovalent attractive force between atoms, molecules, and/or ions

internal energy (U) | total of all possible kinds of energy present in a substance or substances

internal radiation therapy | (also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

interstitial sites | spaces between the regular particle positions in any array of atoms or ions

ion | electrically charged atom or molecule (contains unequal numbers of protons and electrons)

ion pair | solvated anion/cation pair held together by moderate electrostatic attraction

ion-dipole attraction | electrostatic attraction between an ion and a polar molecule

ion-product constant for water (K_w) | equilibrium constant for the autoionization of water

ionic bond | electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic bond | strong electrostatic force of attraction between cations and anions in an ionic compound

ionic compound | compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

ionic solid | solid composed of positive and negative ions held together by strong electrostatic attractions

ionization energy | energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

ionization isomer | (or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

ionizing radiation | radiation that can cause a molecule to lose an electron and form an ion

isoelectronic | group of ions or atoms that have identical electron configurations

isomers | compounds with the same chemical formula but different structures

isomorphous | possessing the same crystalline structure

isotonic | of equal osmotic pressure

isotopes | atoms that contain the same number of protons but different numbers of neutrons

J

joule (J) | SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

K

K_c | equilibrium constant for reactions based on concentrations of reactants and products

kelvin (K) | SI unit of temperature; 273.15 K = 0 °C

kilogram (kg) | standard SI unit of mass; 1 kg = approximately 2.2 pounds

kinetic energy | energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

K_P | equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

L

lanthanide | inner transition metal in the top of the bottom two rows of the periodic table

lanthanide series | (also, lanthanoid series) lanthanum and the elements in the first row or the *f*-block, atomic numbers 57–71

lattice energy ($\Delta H_{\text{lattice}}$) | energy required to separate one mole of an ionic solid into its component gaseous ions

law | statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

law of conservation of matter | when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

law of constant composition | (also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

law of definite proportions | (also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

law of mass action | when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

law of multiple proportions | when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

Le Chatelier's principle | when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

length | measure of one dimension of an object

leveling effect of water | any acid stronger than $\mathrm{H_3O^+}$, or any base stronger than $\mathrm{OH^-}$ will react with water to form $\mathrm{H_3O^+}$, or $\mathrm{OH^-}$, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

Lewis structure | diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol | symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

ligand | ion or neutral molecule attached to the central metal ion in a coordination compound

limiting reactant | reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

line spectrum | electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

linear | shape in which two outside groups are placed on opposite sides of a central atom

linkage isomer | coordination compound that possesses a ligand that can bind to the transition metal in two different ways ($\mathrm{CN^-}$ vs. $\mathrm{NC^-}$)

liquid | state of matter that has a definite volume but indefinite shape

liter (L) | (also, cubic decimeter) unit of volume; 1 L = 1,000 $\mathrm{cm^3}$

lone pair | two (a pair of) valence electrons that are not used to form a covalent bond

low-spin complex | complex in which the electrons minimize the total electron spin by pairing in the lower-energy orbitals before populating the higher-energy orbitals

M

macroscopic domain | realm of everyday things that are large enough to sense directly by human sight and touch

magic number | nuclei with specific numbers of nucleons that are within the band of stability

magnetic quantum number (m_l) | quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of m_l but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field

main-group element | (also, representative element) element in columns 1, 2, and 12–18

manometer | device used to measure the pressure of a gas trapped in a container

mass | fundamental property indicating amount of matter

mass defect | difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass “lost” when nucleons are brought together to form a nucleus)

mass number (A) | sum of the numbers of neutrons and protons in the nucleus of an atom

mass percentage | ratio of solute-to-solution mass expressed as a percentage

mass-energy equivalence equation | Albert Einstein’s relationship showing that mass and energy are equivalent

mass-volume percent | ratio of solute mass to solution volume, expressed as a percentage

matter | anything that occupies space and has mass

melting | change from a solid state to a liquid state

melting point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

metal | element that is shiny, malleable, good conductor of heat and electricity

metal (representative) | atoms of the metallic elements of groups 1, 2, 12, 13, 14, 15, and 16, which form ionic compounds by losing electrons from their outer *s* or *p* orbitals

metallic solid | solid composed of metal atoms

metalloid | element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

metalloid | element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors

meter (m) | standard metric and SI unit of length; 1 m = approximately 1.094 yards

method of initial rates | use of a more explicit algebraic method to determine the orders in a rate law

microscopic domain | realm of things that are much too small to be sensed directly

microstate (*W*) | possible configuration or arrangement of matter and energy within a system

millicurie (mCi) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

milliliter (mL) | 1/1,000 of a liter; equal to 1 cm^3

miscible | mutually soluble in all proportions; typically refers to liquid substances

mixture | matter that can be separated into its components by physical means

molality (*m*) | a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

molar mass | mass in grams of 1 mole of a substance

molar solubility | solubility of a compound expressed in units of moles per liter (mol/L)

molarity (*M*) | unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

mole | amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of ^{12}C

molecular compound | (also, covalent compound) composed of molecules formed by atoms of two or more different elements

molecular equation | chemical equation in which all reactants and products are represented as neutral substances

molecular formula | formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

molecular solid | solid composed of neutral molecules held together by intermolecular forces of attraction

molecular structure | arrangement of atoms in a molecule or ion

molecular structure | structure that includes only the placement of the atoms in the molecule

molecule | bonded collection of two or more atoms of the same or different elements

monatomic ion | ion composed of a single atom

monodentate | ligand that attaches to a central metal through just one coordinate covalent bond

monoprotic acid | acid containing one ionizable hydrogen atom per molecule

multiple equilibrium | system characterized by more than one state of balance between a slightly soluble ionic solid and an aqueous solution of ions working simultaneously

N

Nernst equation | equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

net ionic equation | chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

neutral | describes a solution in which $[H_3O^+] = [OH^-]$

neutron | uncharged, subatomic particle located in the nucleus

nitrate | NO_3^- ion; salt of nitric acid

nitrogen fixation | formation of nitrogen compounds from molecular nitrogen

noble gas | (also, inert gas) element in group 18

node | any point of a standing wave with zero amplitude

node | plane separating different lobes of orbitals, where the probability of finding an electron is zero

nomenclature | system of rules for naming objects of interest

nonelectrolyte | substance that does not produce ions when dissolved in water

nonionizing radiation | radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules

nonmetal | element that appears dull, poor conductor of heat and electricity

nonspontaneous process | process that requires continual input of energy from an external source

normal boiling point | temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

nuclear binding energy | energy lost when an atom's nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

nuclear chemistry | study of the structure of atomic nuclei and processes that change nuclear structure

nuclear fuel | fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

nuclear moderator | substance that slows neutrons to a speed low enough to cause fission

nuclear reaction | change to a nucleus resulting in changes in the atomic number, mass number, or energy state

nuclear reactor | environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

nuclear transmutation | conversion of one nuclide into another nuclide

nucleon | collective term for protons and neutrons in a nucleus

nucleus | massive, positively charged center of an atom made up of protons and neutrons

nuclide | nucleus of a particular isotope

nutritional calorie (Calorie) | unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

O

octahedral | shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

octahedral hole | open space in a crystal at the center of six particles located at the corners of an octahedron

octet rule | guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

optical isomer | (also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

orbital diagram | pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

organic compound | natural or synthetic compound that contains carbon

osmosis | diffusion of solvent molecules through a semipermeable membrane

osmotic pressure (Π) | opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Ostwald process | industrial process used to convert ammonia into nitric acid

overall reaction order | sum of the reaction orders for each substance represented in the rate law

overlap | coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

oxidation half-reaction | the "half" of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

oxide | binary compound of oxygen with another element or group, typically containing O^{2-} ions or the group –O– or =O

oxyacid | compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

oxyacid | compound containing a nonmetal and one or more hydroxyl groups

oxyanion | polyatomic anion composed of a central atom bonded to oxygen atoms

ozone | allotrope of oxygen; O_3

P

***p* orbital** | dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$. An electron in this orbital is called a *p* electron

pairing energy (P) | energy required to place two electrons with opposite spins into a single orbital

parent nuclide | unstable nuclide that changes spontaneously into another (daughter) nuclide

partially miscible | of moderate mutual solubility; typically refers to liquid substances

particle accelerator | device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

parts per billion (ppb) | ratio of solute-to-solution mass multiplied by 10^9

parts per million (ppm) | ratio of solute-to-solution mass multiplied by 10^6

pascal (Pa) | SI unit of pressure; 1 Pa = 1 N/m^2

passivation | metals with a protective nonreactive film of oxide or other compound that creates a barrier for chemical reactions; physical or chemical removal of the passivating film allows the metals to demonstrate their expected chemical reactivity

Pauli exclusion principle | specifies that no two electrons in an atom can have the same value for all four quantum numbers

percent composition | percentage by mass of the various elements in a compound

percent ionization | ratio of the concentration of the ionized acid to the initial acid concentration, times 100

percent yield | measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

period | (also, series) horizontal row of the periodic table

periodic law | properties of the elements are periodic function of their atomic numbers.

periodic table | table of the elements that places elements with similar chemical properties close together

peroxide | molecule containing two oxygen atoms bonded together or as the anion, O_2^{2-}

pH | logarithmic measure of the concentration of hydronium ions in a solution

phase diagram | pressure-temperature graph summarizing conditions under which the phases of a substance can exist

photon | smallest possible packet of electromagnetic radiation, a particle of light

photosynthesis | process whereby light energy promotes the reaction of water and carbon dioxide to form carbohydrates and oxygen; this allows photosynthetic organisms to store energy

physical change | change in the state or properties of matter that does not involve a change in its chemical composition

physical property | characteristic of matter that is not associated with any change in its chemical composition

pi bond (π bond) | covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

Pidgeon process | chemical reduction process used to produce magnesium through the thermal reaction of magnesium oxide with silicon

plasma | gaseous state of matter containing a large number of electrically charged atoms and/or molecules

platinum metals | group of six transition metals consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum that tend to occur in the same minerals and demonstrate similar chemical properties

pnictogen | element in group 15

pOH | logarithmic measure of the concentration of hydroxide ions in a solution

polar covalent bond | covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

polar molecule | (also, dipole) molecule with an overall dipole moment

polarizability | measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

polyatomic ion | ion composed of more than one atom

polydentate ligand | ligand that is attached to a central metal ion by bonds from two or more donor atoms, named with prefixes specifying how many donors are present (e.g., hexadentate = six coordinate bonds formed)

polymorph | variation in crystalline structure that results in different physical properties for the resulting compound

position of equilibrium | concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

positron ($_{+1}^{0}\beta$ or $_{+1}^{0}e$) | antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

positron emission | (also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

potential energy | energy of a particle or system of particles derived from relative position, composition, or condition

pounds per square inch (psi) | unit of pressure common in the US

precision | how closely a measurement matches the same measurement when repeated

pressure | force exerted per unit area

principal quantum number (*n*) | quantum number specifying the shell an electron occupies in an atom

product | substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

proton | positively charged, subatomic particle located in the nucleus

pure covalent bond | (also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

pure substance | homogeneous substance that has a constant composition

Q

quantitative analysis | the determination of the amount or concentration of a substance in a sample

quantization | occurring only in specific discrete values, not continuous

quantum mechanics | field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

quantum number | integer number having only specific allowed values and used to characterize the arrangement of electrons in an atom

R

radiation absorbed dose (rad) | SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy

radiation dosimeter | device that measures ionizing radiation and is used to determine personal radiation exposure

radiation therapy | use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive decay | spontaneous decay of an unstable nuclide into another nuclide

radioactive decay series | chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

radioactive tracer | (also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

radioactivity | phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

radiocarbon dating | highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of $^{14}_{6}\mathrm{C}:\ ^{12}_{6}\mathrm{C}$ in the object vs. the ratio of $^{14}_{6}\mathrm{C}:\ ^{12}_{6}\mathrm{C}$ in the present-day atmosphere

radioisotope | isotope that is unstable and undergoes conversion into a different, more stable isotope

radiometric dating | use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

Raoult's law | the partial pressure exerted by a solution component is equal to the product of the component's mole fraction in the solution and its equilibrium vapor pressure in the pure state

rare earth element | collection of 17 elements including the lanthanides, scandium, and yttrium that often occur together and have similar chemical properties, making separation difficult

rate constant (*k*) | proportionality constant in the relationship between reaction rate and concentrations of reactants

rate expression | mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

rate law | (also, rate equation) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

rate of reaction | measure of the speed at which a chemical reaction takes place

reactant | substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

reaction order | value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

reaction quotient (Q) | ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

reactor coolant | assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

reduction half-reaction | the “half” of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

relative biological effectiveness (RBE) | measure of the relative damage done by radiation

representative element | (also, main-group element) element in columns 1, 2, and 12–18

representative element | element where the *s* and *p* orbitals are filling

representative metal | metal among the representative elements

resonance | situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms | two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid | average of the resonance forms shown by the individual Lewis structures

reversible process | process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

reversible reaction | chemical reaction that can proceed in both the forward and reverse directions under given conditions

roentgen equivalent man (rem) | unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv

rounding | procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

S

s orbital | spherical region of space with high electron density, describes orbitals with $l = 0$. An electron in this orbital is called an s electron

sacrificial anode | more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

saturated | of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

saturated hydrocarbon | molecule containing carbon and hydrogen that has only single bonds between carbon atoms

scientific method | path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory

scintillation counter | instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation

second (s) | SI unit of time

second law of thermodynamics | entropy of the universe increases for a spontaneous process

second transition series | transition elements in the fifth period of the periodic table (second row of the *d*-block), atomic numbers 39–47

selective precipitation | process in which ions are separated using differences in their solubility with a given precipitating reagent

semipermeable membrane | a membrane that selectively permits passage of certain ions or molecules

series | (also, period) horizontal row of the period table

shell | set of orbitals with the same principal quantum number, *n*

SI units (International System of Units) | standards fixed by international agreement in the International System of Units (*Le Système International d’Unités*)

sievert (Sv) | SI unit measuring tissue damage caused by radiation; takes into account energy and biological effects of radiation

sigma bond (σ bond) | covalent bond formed by overlap of atomic orbitals along the internuclear axis

significant figures | (also, significant digits) all of the measured digits in a determination, including the uncertain last digit

silicate | compound containing silicon-oxygen bonds, with silicate tetrahedra connected in rings, sheets, or three-dimensional networks, depending on the other elements involved in the formation of the compounds

simple cubic structure | crystalline structure with a cubic unit cell with lattice points only at the corners

simple cubic unit cell | (also, primitive cubic unit cell) unit cell in the simple cubic structure

single bond | bond in which a single pair of electrons is shared between two atoms

skeletal structure | shorthand method of drawing organic molecules in which carbon atoms are represented by the ends of lines and bends in between lines, and hydrogen atoms attached to the carbon atoms are not shown (but are understood to be present by the context of the structure)

smelting | process of extracting a pure metal from a molten ore

solid | state of matter that is rigid, has a definite shape, and has a fairly constant volume

solubility | extent to which a solute may be dissolved in water, or any solvent

solubility product (K_{sp}) | equilibrium constant for the dissolution of a slightly soluble electrolyte

solute | solution component present in a concentration less than that of the solvent

solvation | exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

solvent | solution component present in a concentration that is higher relative to other components

space lattice | all points within a crystal that have identical environments

spatial isomers | compounds in which the relative orientations of the atoms in space differ

specific heat capacity (*c*) | intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

spectator ion | ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

spectrochemical series | ranking of ligands according to the magnitude of the crystal field splitting they induce

spin quantum number (m_s) | number specifying the electron spin direction, either $+\frac{1}{2}$ or $-\frac{1}{2}$

spontaneous change | process that takes place without a continuous input of energy from an external source

spontaneous process | physical or chemical change that occurs without the addition of energy from an external source

standard cell potential (E°_{cell}) | the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

standard enthalpy of combustion (ΔH°_c) | heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation (ΔH°_f) | enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard entropy (S°) | entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S°_{298}

standard entropy change (ΔS°) | change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS°_{298}

standard free energy change (Δ*G*°) | change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG°_f) | change in free energy accompanying the formation of one mole of substance from its elements in their standard states

standard hydrogen electrode (SHE) | the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

standard reduction potential (*E*°) | the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

standard state | set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

standing wave | (also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

state function | property depending only on the state of a system, and not the path taken to reach that state

steel | material made from iron by removing impurities in the iron and adding substances that produce alloys with properties suitable for specific uses

stepwise ionization | process in which an acid is ionized by losing protons sequentially

stress | change to a reaction's conditions that may cause a shift in the equilibrium

strong electrolyte | substance that dissociates or ionizes completely when dissolved in water

strong nuclear force | force of attraction between nucleons that holds a nucleus together

strong-field ligand | ligand that causes larger crystal field splittings

structural formula | shows the atoms in a molecule and how they are connected

structural isomer | one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

subcritical mass | amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

sublimation | change from solid state directly to gaseous state

subshell | set of orbitals in an atom with the same values of *n* and *l*

substituent | branch or functional group that replaces hydrogen atoms in a larger hydrocarbon chain

substitution reaction | reaction in which one atom replaces another in a molecule

sulfate | SO_4^{2-} ion

sulfite | SO_3^{2-} ion

superconductor | material that conducts electricity with no resistance

supercritical fluid | substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

supercritical mass | amount of material in which there is an increasing rate of fission

superoxide | oxide containing the anion O_2^-

supersaturated | of concentration that exceeds solubility; a nonequilibrium state

surface tension | energy required to increase the area, or length, of a liquid surface by a given amount

surroundings | all matter other than the system being studied

symbolic domain | specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

system | portion of matter undergoing a chemical or physical change being studied

T

***t_{2g}* orbitals** | set of three *d* orbitals aligned between the Cartesian axes for coordination complexes; in octahedral complexes, they are lowered in energy compared to the e_g orbitals according to CFT

temperature | intensive property of matter that is a quantitative measure of “hotness” and “coldness”

tetrahedral | shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

tetrahedral hole | tetrahedral space formed by four atoms or ions in a crystal

theoretical yield | amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

theory | well-substantiated, comprehensive, testable explanation of a particular aspect of nature

thermal energy | kinetic energy associated with the random motion of atoms and molecules

thermochemistry | study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

third law of thermodynamics | entropy of a perfect crystal at absolute zero (0 K) is zero

third transition series | transition elements in the sixth period of the periodic table (third row of the *d*-block), atomic numbers 57 and 72–79

titrant | solution containing a known concentration of substance that will react with the analyte in a titration analysis

titration analysis | quantitative chemical analysis method that involves measuring the volume of a reactant solution required to completely react with the analyte in a sample

titration curve | plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

torr | unit of pressure; $1\ \text{torr} = \frac{1}{760}\ \text{atm}$

***trans* configuration** | configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

transition metal | element in columns 3–11

transmutation reaction | bombardment of one type of nuclei with other nuclei or neutrons

transuranium element | element with an atomic number greater than 92; these elements do not occur in nature

trigonal bipyramidal | shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar | shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

triple bond | bond in which three pairs of electrons are shared between two atoms

triple point | temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

triprotic acid | acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

Tyndall effect | scattering of visible light by a colloidal dispersion

U

uncertainty | estimate of amount by which measurement differs from true value

unified atomic mass unit (u) | alternative unit equivalent to the atomic mass unit

unit | standard of comparison for measurements

unit cell | smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

unit conversion factor | ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

unsaturated | of concentration less than solubility

V

vacancy | defect that occurs when a position that should contain an atom or ion is vacant

valence bond theory | description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

valence electrons | electrons in the outermost or valence shell (highest value of *n*) of a ground-state atom; determine how an element reacts

valence shell | outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest *n* level (*s* and *p* subshells) are in the valence shell, while for transition metals, the highest energy *s* and *d* subshells make up the valence shell and for inner transition elements, the highest *s*, *d,* and *f* subshells are included

valence shell electron-pair repulsion theory (VSEPR) | theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

van der Waals equation | modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

van der Waals force | attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

van't Hoff factor (*i*) | the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

vapor pressure | (also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

vaporization | change from liquid state to gaseous state

vector | quantity having magnitude and direction

viscosity | measure of a liquid's resistance to flow

voltaic cell | another name for a galvanic cell

volume | amount of space occupied by an object

volume percentage | ratio of solute-to-solution volume expressed as a percentage

W

wave | oscillation that can transport energy from one point to another in space

wave-particle duality | term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

wavefunction (*ψ*) | mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

wavelength (*λ*) | distance between two consecutive peaks or troughs in a wave

weak electrolyte | substance that ionizes only partially when dissolved in water

weak-field ligand | ligand that causes small crystal field splittings

weight | force that gravity exerts on an object

work (*w*) | energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

X

X-ray crystallography | experimental technique for determining distances between atoms in a crystal by measuring the angles at which X-rays are diffracted when passing through the crystal

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