GENERAL CHEMISTRY



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General Chemistry

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1: MATTER- ITS PROPERTIES AND MEASUREMENT

Petrucci: *General Chemistry*
Principles and Modern Applications

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1.1: The Scientific Method

Learning Objectives

- To identify the components of the scientific method

Scientists search for answers to questions and solutions to problems by using a procedure called the **scientific method**. This procedure consists of making observations, formulating hypotheses, and designing experiments, which in turn lead to additional observations, hypotheses, and experiments in repeated cycles (Figure 1.1.1).

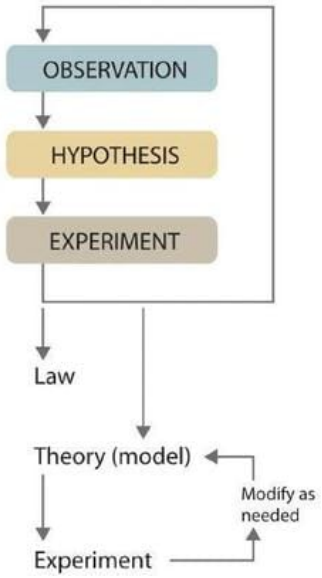


Figure 1.1.1: The Scientific Method. As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

Observations can be qualitative or quantitative. Qualitative observations describe properties or occurrences in ways that do not rely on numbers. Examples of qualitative observations include the following: the outside air temperature is cooler during the winter season, table salt is a crystalline solid, sulfur crystals are yellow, and dissolving a penny in dilute nitric acid forms a blue solution and a brown gas. Quantitative observations are measurements, which by definition consist of both a number and a unit. Examples of quantitative observations include the following: the melting point of crystalline sulfur is 115.21 °C, and 35.9 grams of table salt—whose chemical name is sodium chloride—dissolve in 100 grams of water at 20 °C. An example of a quantitative observation was the initial observation leading to the modern theory of the dinosaurs' extinction: iridium concentrations in sediments dating to 66 million years ago were found to be 20–160 times higher than normal. The development of this theory is a good exemplar of the scientific method in action (see Figure 1.1.2 below).

After deciding to learn more about an observation or a set of observations, scientists generally begin an investigation by forming a **hypothesis**, a tentative explanation for the observation(s). The hypothesis may not be correct, but it puts the scientist's understanding of the system being studied into a form that can be tested. For example, the observation that we experience alternating periods of light and darkness corresponding to observed movements of the sun, moon, clouds, and shadows is consistent with either of two hypotheses:

1. Earth rotates on its axis every 24 hours, alternately exposing one side to the sun, or
2. The sun revolves around Earth every 24 hours.

Suitable experiments can be designed to choose between these two alternatives. For the disappearance of the dinosaurs, the hypothesis was that the impact of a large extraterrestrial object caused their extinction. Unfortunately (or perhaps fortunately), this hypothesis does not lend itself to direct testing by any obvious experiment, but scientists collected additional data that either support or refute it.

After a hypothesis has been formed, scientists conduct experiments to test its validity. **Experiments** are systematic observations or measurements, preferably made under controlled conditions—that is, under conditions in which a single variable changes. For example, in the dinosaur extinction scenario, iridium concentrations were measured worldwide and compared. A properly designed and executed experiment enables a scientist to determine whether the original hypothesis is valid. Experiments often demonstrate that the hypothesis is incorrect or that it must be modified. More experimental data are then collected and analyzed, at which point a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in a **law**, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply says what happens; it does not address the question of why.

One example of a law, the Law of Definite Proportions, which was discovered by the French scientist Joseph Proust (1754–1826), states that a chemical substance always contains the same proportions of elements by mass. Thus sodium chloride (table salt) always contains the same proportion by mass of sodium to chlorine, in this case 39.34% sodium and 60.66% chlorine by mass, and sucrose (table sugar) is always 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass. Some solid compounds do not strictly obey the law of definite proportions. The law of definite proportions should seem obvious—we would expect the composition of sodium chloride to be consistent—but the head of the US Patent Office did not accept it as a fact until the early 20th century.

Whereas a law states only what happens, a **theory** attempts to explain why nature behaves as it does. Laws are unlikely to change greatly over time unless a major experimental error is discovered. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered. The theory developed to explain the extinction of the dinosaurs, for example, is that Earth occasionally encounters small- to medium-sized asteroids, and these encounters may have unfortunate implications for the continued existence of most species. This theory is by no means proven, but it is consistent with the bulk of evidence amassed to date. Figure 1.1.2 summarizes the application of the scientific method in this case.

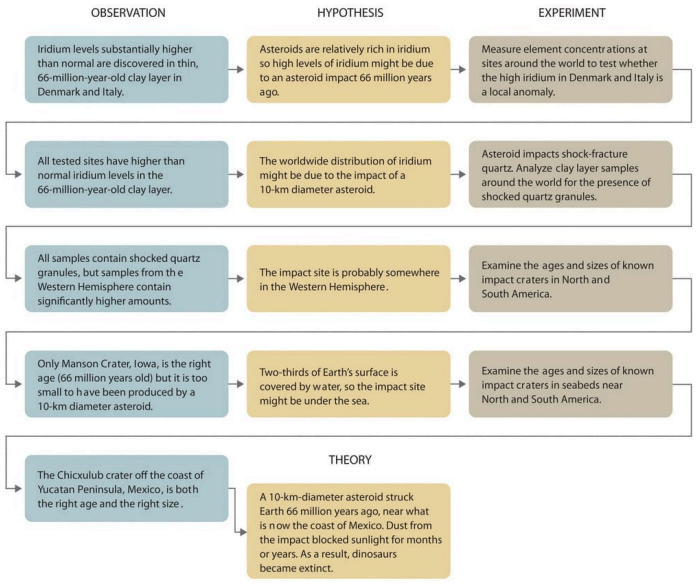


Figure 1.1.2: A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth

Example 1.1.1

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Ice always floats on liquid water.
b. Birds evolved from dinosaurs.
c. Hot air is less dense than cold air, probably because the components of hot air are moving more rapidly.
d. When 10 g of ice were added to 100 mL of water at 25 °C, the temperature of the water decreased to 15.5 °C after the ice melted.
e. The ingredients of Ivory soap were analyzed to see whether it really is 99.44% pure, as advertised.

Given: components of the scientific method

Asked for: statement classification

Strategy: Refer to the definitions in this section to determine which category best describes each statement.

Solution

a. This is a general statement of a relationship between the properties of liquid and solid water, so it is a law.
b. This is a possible explanation for the origin of birds, so it is a hypothesis.
c. This is a statement that tries to explain the relationship between the temperature and the density of air based on fundamental principles, so it is a theory.
d. The temperature is measured before and after a change is made in a system, so these are quantitative observations.
e. This is an analysis designed to test a hypothesis (in this case, the manufacturer's claim of purity), so it is an experiment.

Exercise 1.1.1

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Measured amounts of acid were added to a Rolaids tablet to see whether it really "consumes 47 times its weight in excess stomach acid."
b. Heat always flows from hot objects to cooler ones, not in the opposite direction.
c. The universe was formed by a massive explosion that propelled matter into a vacuum.
d. Michael Jordan is the greatest pure shooter ever to play professional basketball.
e. Limestone is relatively insoluble in water but dissolves readily in dilute acid with the evolution of a gas.
f. Gas mixtures that contain more than 4% hydrogen in air are potentially explosive.

Answer a available at the end of this section.

Because scientists can enter the cycle shown in Figure 1.1.1 at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

It is important to remember that scientists have a tendency to formulate hypotheses in familiar terms simply because it is difficult to propose something that has never been encountered or imagined before. As a result, scientists sometimes discount or overlook unexpected findings that disagree with the basic assumptions behind the hypothesis or theory being tested. Fortunately, truly important findings are immediately subject to independent verification by scientists in other laboratories, so science is a self-correcting discipline. When the Alvarezes originally suggested that an extraterrestrial impact caused the extinction of the dinosaurs, the response was almost universal skepticism and scorn. In only 20 years, however, the persuasive nature of the evidence overcame the skepticism of many scientists, and their initial hypothesis has now evolved into a theory that has revolutionized paleontology and geology.

Summary

Chemists expand their knowledge by making observations, carrying out experiments, and testing hypotheses to develop laws to summarize their results and theories to explain them. In doing so, they are using the scientific method.

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Answers

Exercise 1.1.1

experiment
law
theory
hypothesis
qualitative observation
quantitative observation

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1.2: 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 1.2.1). 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.

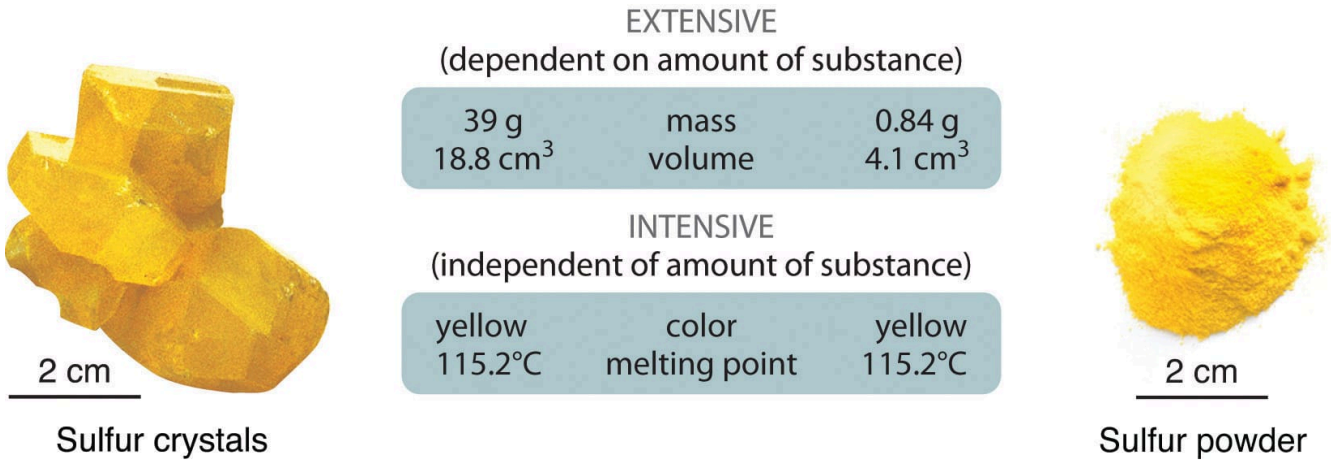


Figure 1.2.1: The Difference between Extensive and Intensive Properties of Matter. Because they differ in size, the two samples of sulfur have different extensive properties, such as mass and volume. In contrast, their intensive properties, including color, melting point, and electrical conductivity, 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:

$$density = \frac{mass}{volume} \rightarrow \rho = \frac{m}{v} \tag{1.2.1}$$

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 1.2.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table 1.2.1: Densities of Common Substances

Substance	Density at 25°C (g/cm3)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

Physical Property and Change

Change in which the matter's physical appearance is altered, but composition remains unchanged, e.g., a change in state of matter. The three main states of matter are: Solid, Liquid, Gas

- Solid is distinguished by a fixed structure. Its shape and volume do not change. In a solid, atoms are tightly packed together in a fixed arrangement.
- Liquid is distinguished by its malleable shape (is able to form into the shape of its container), but constant volume. In a liquid, atoms are close together but not in a fixed arrangement.
- Gas is made up of atoms that are separate. However, unlike solid & liquid, a gas has no fixed shape and volume.

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Different Definitions of Properties: https://youtu.be/n7UwjQJGh9Y

Example 1.2.1: Physical Change

When liquid water (H_2O) freezes into a solid state (ice), 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.



Figure 1.2.2: Ice Melting is a physical change

Chemical Properties and Change

- **Chemical Property is** Any characteristic that gives a sample of matter the ability/inability to undergo a change that alters its composition. Examples: Alkali metals react with water; Paper's ability to burn.
- **Chemical Change is a** Change in which one or more kinds of matter are transformed to new kinds of matter with altered compositions (or Chemical Reaction).

Example 1.2.2: Chemical Change

The combustion of magnetisum metal is a chemical change (Magnesium + Oxygen → Magnesium Oxide):

$$2Mg + O_2 \rightarrow 2MgO \tag{1.2.2}$$

The rusting of iron is a chemical change (Iron + Oxygen → Iron Oxide/ Rust):

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \tag{1.2.3}$$

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

YouTube Video

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Different Definitions of Changes: https://youtu.be/OiLaMHigCuo

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1.3: 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.

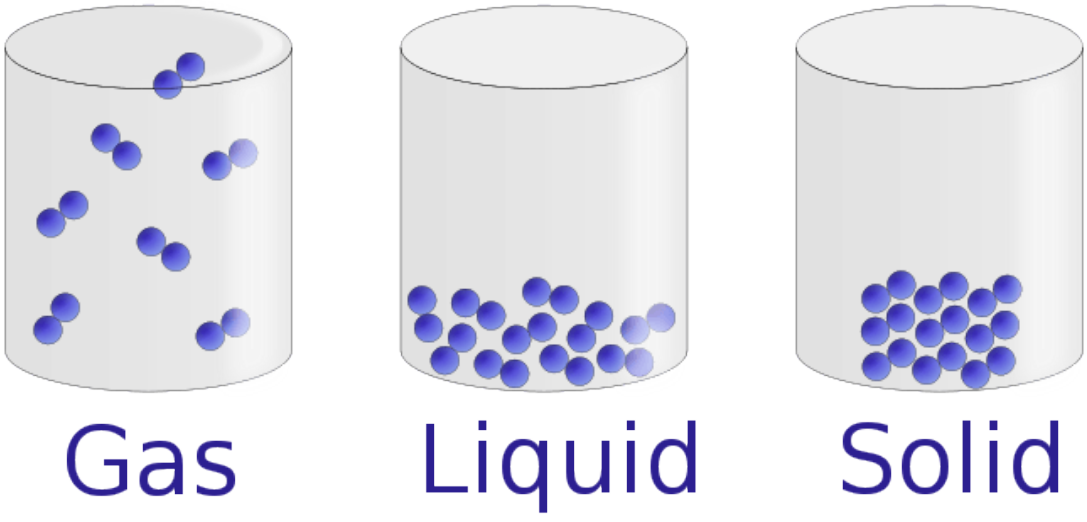


Figure 1.3.1: The Three States of Matter. Solids have a defined shape and volume. Liquids have a fixed volume but flow to assume the shape of their containers. Gases completely fill their containers, regardless of volume. Figure used with permission from Wikipedia

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 1.3.2: 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.

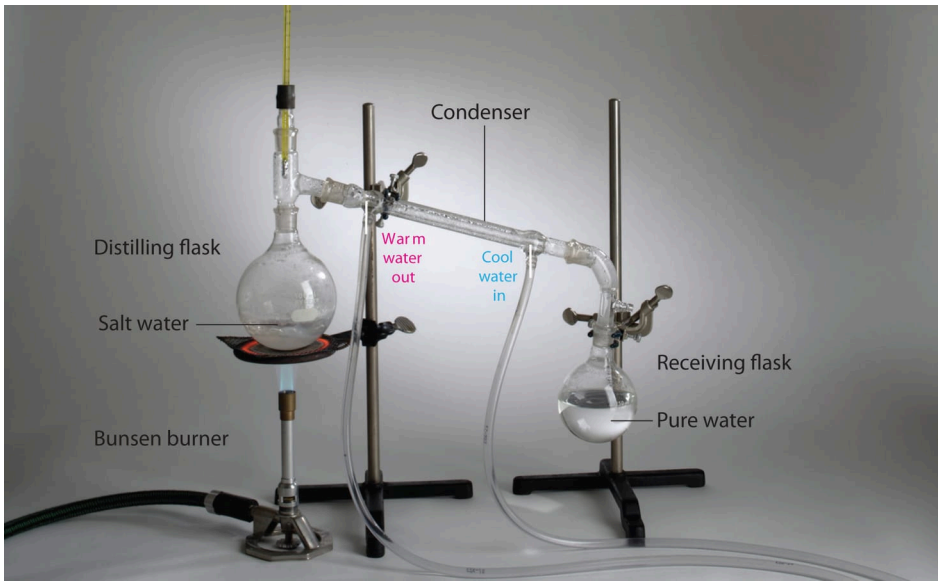


Figure 1.3.3: The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving 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 1.3.4: 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: https://www.youtube.com/watch?v=BLq5NibwV5g

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 115 elements are known, but millions of chemical compounds have been prepared from these 115 elements. The known elements are listed in the periodic table.

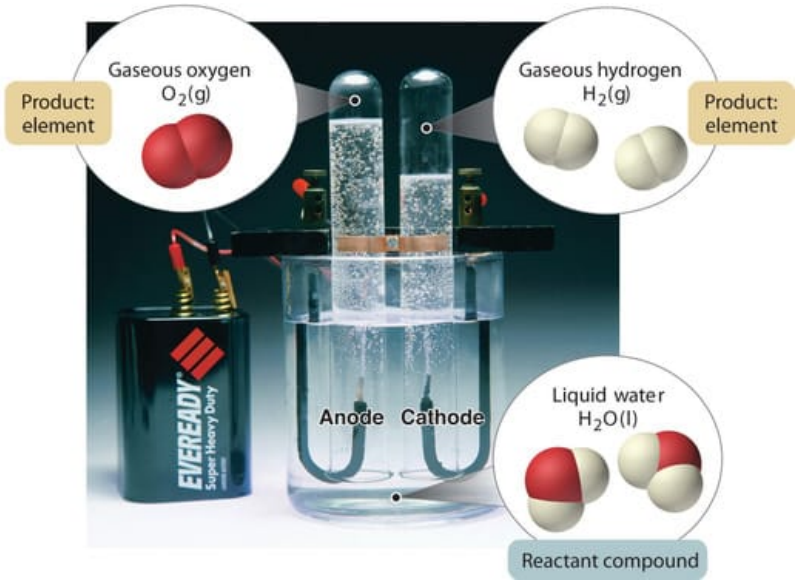


Figure 1.3.5: The Decomposition of Water to Hydrogen and Oxygen by Electrolysis. Water is a chemical compound; hydrogen and oxygen are elements.

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 calledelectrolysis. In electrolysis, electricity provides the energy needed to separate a compound into its constituent elements (Figure 1.3.5). 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 1.3.6.

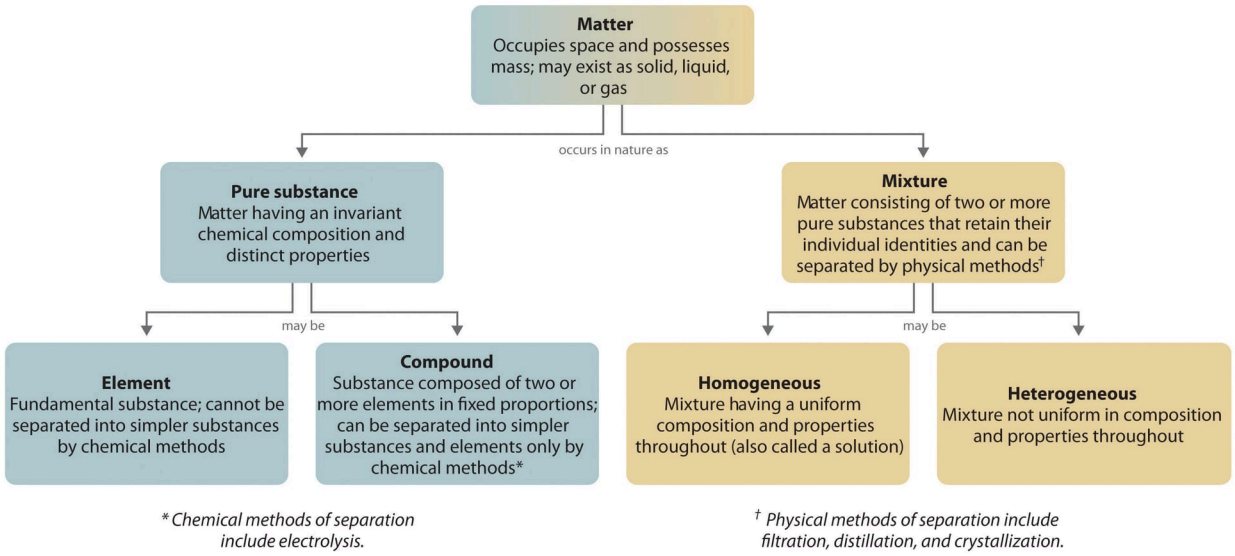


Figure 1.3.6: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

Example 1.3.1

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 1.3.1

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. solution
b. element
c. heterogeneous mixture
d. compound

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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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1.4: Measurement of Matter - SI (Metric) Units

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

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^{18}		deci	s	10^{-1}
tera	T	10^{12}		centi	c	10^{-2}
giga	G	10^{9}		milli	m	10^{-3}

Prefix	Abbreviation	Multiplier		Prefix	Abbreviation	Multiplier
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.

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:

$$V = x \cdot y \cdot z \tag{1.4.1}$$

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

$$dim\{V\} = L^3 \tag{1.4.2}$$

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,

$$dim\{V\} = M^0L^3T^0Q^0\Theta^0 \tag{1.4.3}$$

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

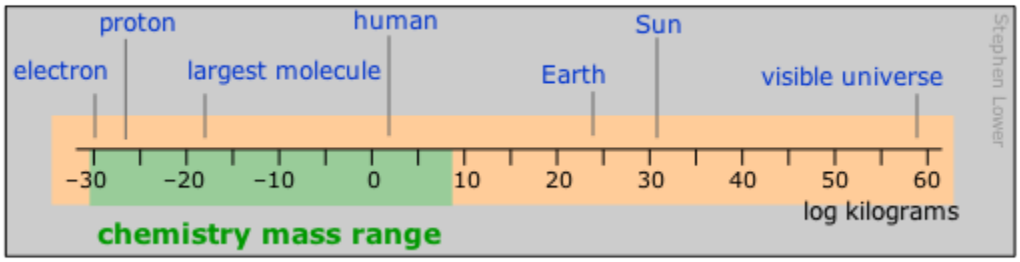
Dimensional analysis is widely employed when it is necessary to convert one kind of unit into another, and chemistry students often use it in "chemical arithmetic" calculations, in which context it is also known as the "Factor-Label" method. In this section, we will look at some of the quantities that 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:

$$f = ma = mg \tag{1.4.4}$$

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.

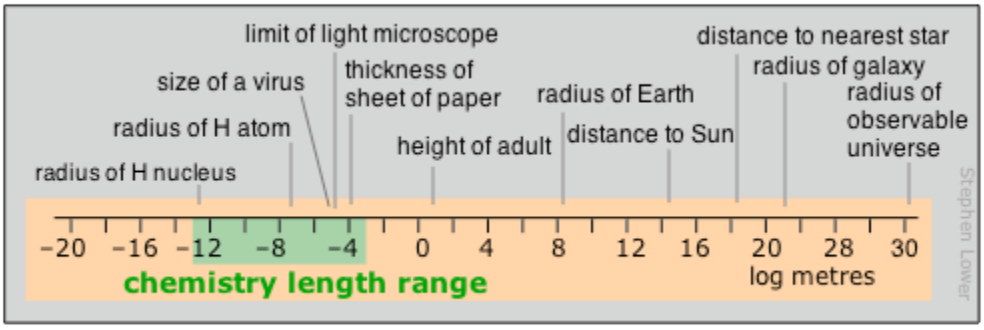


Please note that in this diagram and in those that follow, the numeric scale represents the *logarithm* of the number shown. For example, the mass of the electron is 10^{-30} kg.

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

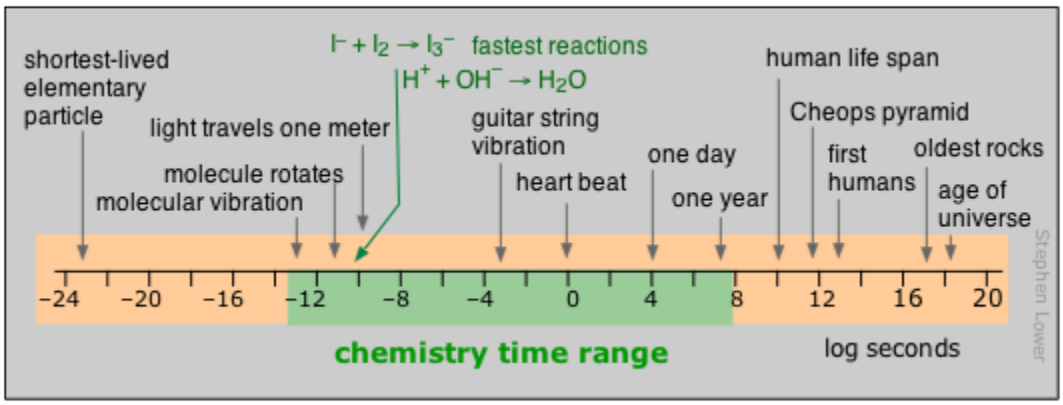
Chemists tend to work mostly in the moderately-small part of the distance range. Those who live in the lilliputian world of crystal- and molecular structures and atomic radii find the *picometer* a convenient currency, but one still sees the older non-SI unit called the *Ångstrom* used in this context; 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.



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

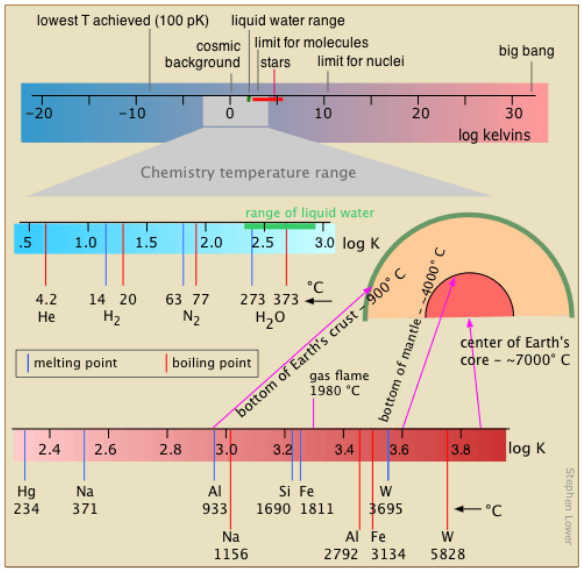
that eventually define our lifetimes. Beyond the few thousands of years of history behind us, those years-to-the-powers-of-tens that are the fare for such fields as evolutionary biology, geology, and cosmology, cease to convey any real meaning for us. Perhaps this is why so many people are not very inclined to accept their validity.



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.



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.

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:

$$1\ Pa = 1\ N\ m^{-2} \tag{1.4.5}$$

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

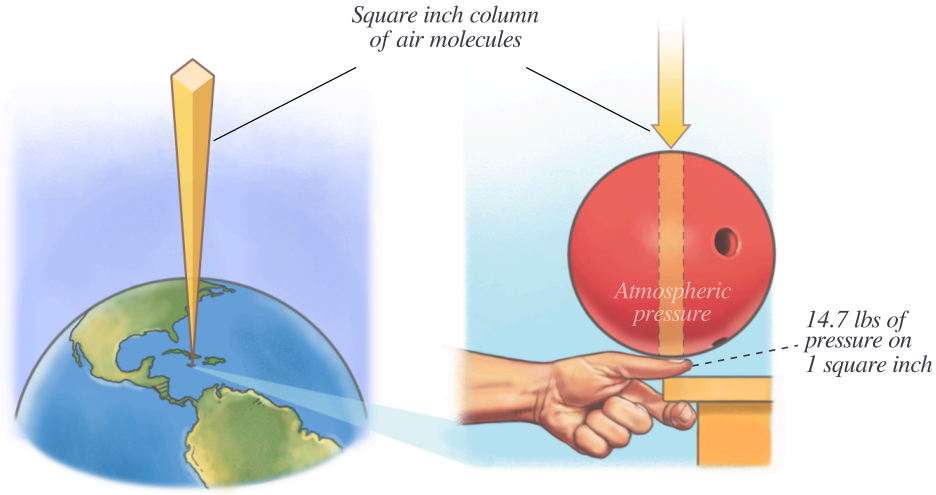


Figure 1.4.1: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail. (CC BY-NC; Ümit Kaya)

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.

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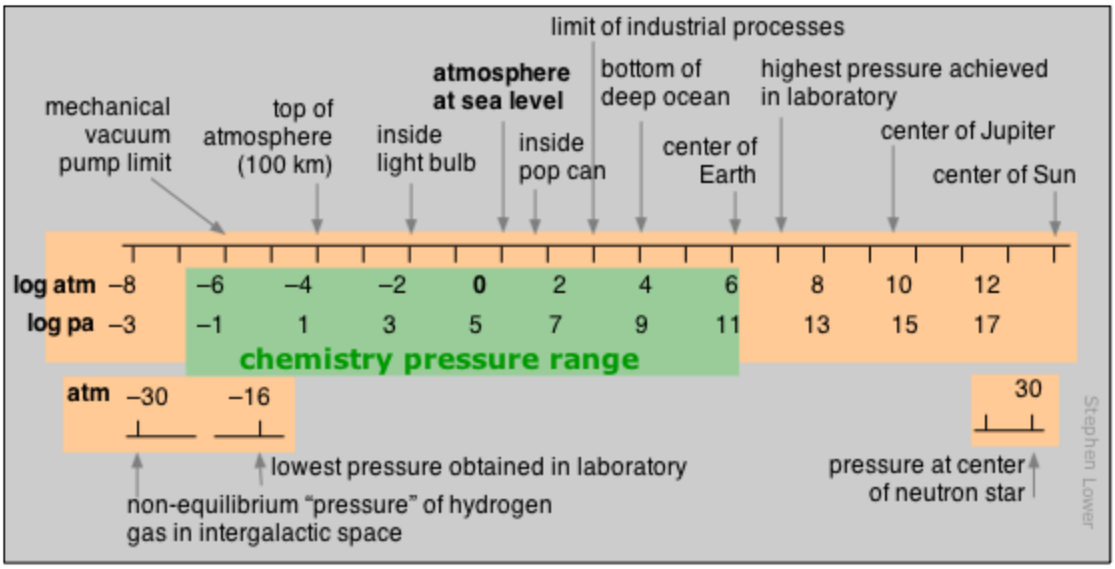
Video 1.4.1: A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased. A smaller scale demonstration of this phenomenon is briefly explained.

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

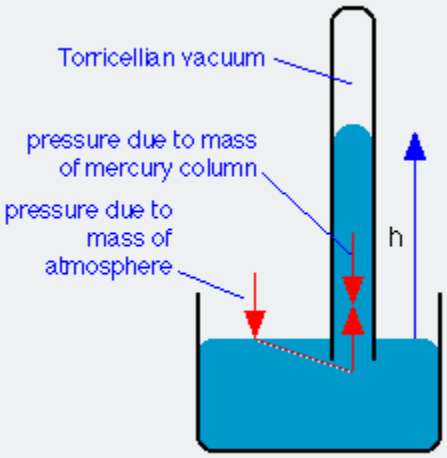
$$f = ma = mg = (10340\ kg)(9.81\ m\ s^{-2}) = 1.013 \times 10^5\ kg\ m\ s^{-2} = 1.013 \times 10^5\ N \tag{1.4.6}$$

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.



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.



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.

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: Density and Percent Composition - Their Use in Problem Solving

Learning Objectives

- To be introduced to the concepts of Density and Percent Composition as important properties of matter.

Density and percent composition are important properties in chemistry. Each have basic components as well as broad applications. Components of density are: mass and volume, both of which can be more confusing than at first glance. An application of the concept of density is determining the volume of an irregular shape using a known mass and density. Determining Percent Composition requires knowing the mass of entire object or molecule and the mass of its components.

Introduction

Which one weighs more, a kilogram of feathers or a kilogram of bricks? Though many people will say that a kilogram of bricks is heavier, they actually weigh the same! However, many people are caught up by the concept of density ρ, which causes them to answer the question incorrectly. A kilogram of feathers clearly takes up more space, but this is because it is less "dense." But what is density, and how can we determine it?

In the laboratory, density can be used to identify an element, while percent composition is used to determine the amount, by mass, of each element present in a chemical compound. In daily life, density explains everything from why boats float to why air bubbles will try to escape from soda. It even affects your health because bone density is very important. Similarly, percent composition is commonly used to make animal feed and compounds such as the baking soda found in your kitchen.

Density

Density is a physical property found by dividing the mass of an object by its volume. Regardless of the sample size, density is always constant. For example, the density of a pure sample of tungsten is always 19.25 grams per cubic centimeter. This means that whether you have one gram or one kilogram of the sample, the density will never vary. The equation, as we already know, is as follows:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \tag{1.5.1}$$

or just

$$\rho = \frac{m}{v} \tag{1.5.2}$$

Based on this equation, it's clear that density can, and does, vary from element to element and substance to substance due to differences in the relation of mass and volume. But let us break it down one step further. What are mass and volume? We cannot understand density until we know its parts: mass and volume. The following two sections will teach you all the information you need to know about volume and mass to properly solve and manipulate the density equation.

Mass

Mass concerns the quantity of matter in an object. The SI unit for mass is the kilogram (kg), although grams (g) are commonly used in the laboratory to measure smaller quantities. Often, people mistake weight for mass. Weight concerns the force exerted on an object as a function of mass and gravity. This can be written as

$$\text{Weight} = \text{mass} \times \text{gravity} \tag{1.5.3}$$

$$Weight = mg$$

Since on the earth, the g in the equation is equal to one, weight and mass are considered equal on earth. It is important to note that although g is equal to one in basic equations, it actually differs throughout earth by a small fraction depending on location; gravity at the equator is less than at the poles. On other astronomical objects, gravity and hence weight, highly differs. This is because weight changes due to variations in gravity and acceleration. The mass, however, of a 1 kg cube will continue to be 1 kg whether it is on the top of a mountain, the bottom of the sea, or on the moon.

Another important difference between mass and weight is how they are measured. Weight is measured with a scale, while mass must be measured with a balance. Just as people confuse mass and weight, they also confuse scales and balances. A balance counteracts the effects of gravity while a scale incorporates it. There are two types of balances found in the laboratory: electronic and manual. With a manual balance, you find the unknown mass of an object by adjusting or comparing known masses until equilibrium is reached. With an electronic balance, which is what you will work with in the UC Davis laboratory, the mass is found by electronic counterbalancing with little effort from the user. An electronic balance can be far more accurate than any other balance and is easier to use, but they are expensive. Also, keep in mind that all instruments used in the laboratory have systematic errors.

Volume

Volume describes the quantity of three dimensional space than an object occupies. The SI unit for volume is meters cubed (m^3), but milliliters (mL), centimeters cubed (cm^3), and liters (L) are more common in the laboratory. There are many equations to find volume. Here are just a few of the easy ones:

$$\text{Volume} = (\text{length})^3$$

or

$$\text{Volume} = (\text{length})(\text{width})(\text{height})$$

or

$$\text{Volume} = (\text{base area})(\text{height})$$

Density: A Further Investigation

Units

We know all of density's components, so let's take a closer look at density itself. The unit most widely used to express density is g/cm^3 or g/mL, though the SI unit for density is technically kg/m^3. Grams per centimeter cubed is equivalent to grams per milliliter (g/cm^3 = g/mL). To solve for density, simply follow the equation 1.5.1. For example, if you had a metal cube with mass 7.00 g and volume 5.00 cm^3, the density would be $\rho = \frac{7\ g}{5\ cm^3} = 1.4\ \ g/cm^3$. Sometimes, you have to convert units to get the correct units for density, such as mg to g or in^3 to cm^3.

Density in the Periodic Table

Density can be used to help identify an unknown element. Of course, you have to know the density of an element with respect to other elements. Below is a table listing the density of a few elements from the Periodic Table at standard conditions for temperature and pressure, or STP. STP corresponds to a temperature of 273 K (0° Celsius) and 1 atmosphere of pressure.

Table 1.5.1: Density of Elements at standard temperature and pressure

Element Name and Symbol	Density (g/cm3)	Atomic Number
Hydrogen (H)	0.09	1
Helium (He)	0.18	2
Aluminum (Al)	2.7	13

Element Name and Symbol	Density (g/cm3)	Atomic Number
Zinc (Zn)	7.13	30
Tin (Sn)	7.31	50
Iron (Fe)	7.87	26
Nickel (Ni)	8.9	28
Cobalt (Co)	8.9	27
Copper (Cu)	8.96	29
Silver (Ag)	10.5	47
Lead (Pb)	11.35	82
Mercury (Hg)	11.55	80
Gold (Au)	19.32	79
Platinum (Pt)	21.45	78
Osmium (Os)	22.6	76

As can be seen from the table, the most dense element is Osmium (Os) with a density of 22.6 g/cm^3. The least dense element is Hydrogen (H) with a density of 0.09 g/cm^3.

Density and Temperature

Density generally decreases with increasing temperature and likewise increases with decreasing temperatures. This is because volume differs according to temperature. Volume increases with increasing temperature. Below is a table showing the density of pure water with differing temperatures.

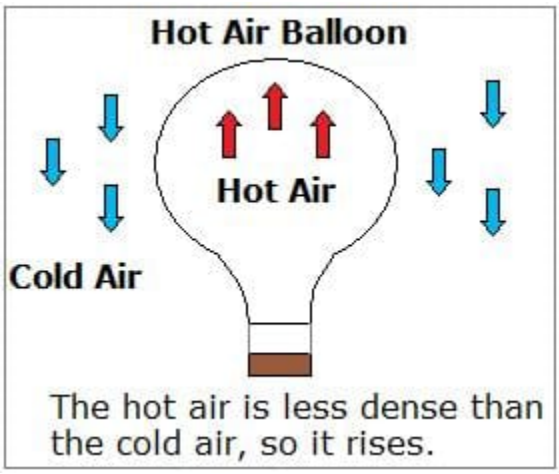
Table 1.5.2: Density fo water as a function of Temperature

Temperature (C)	Density (g/cm3)
100	0.9584
80	0.9718
60	0.9832
40	0.9922
30	0.9957
25	0.997
22	0.9978
20	0.9982
15	0.9991
10	0.9997
4	1.000
0 (liquid)	0.9998
0 (solid)	0.9150

As can be seen from Table 1.5.2, the density of water decreases with increasing temperature. Liquid water also shows an exception to this rule from 0 degrees Celsius to 4 degrees Celsius, where it increases in density instead of decreasing as expected. Looking at the table, you can also see that ice is less dense than water. This is unusual as solids are generally denser than their liquid counterparts. Ice is less dense than water due to hydrogen bonding. In the water molecule, the hydrogen bonds are strong and

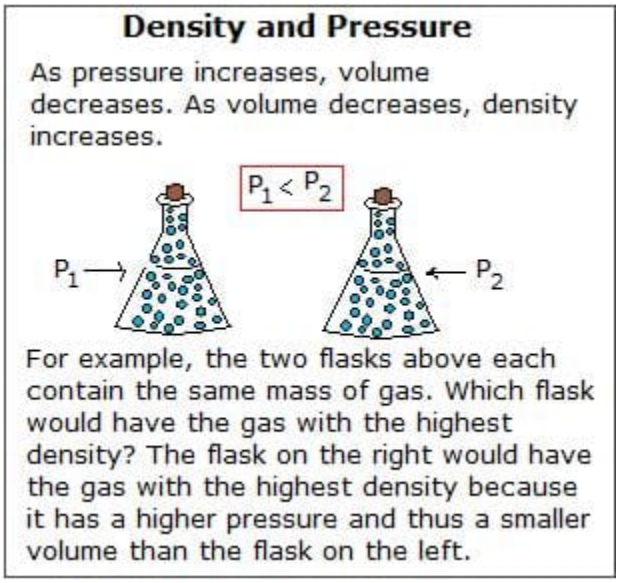
compact. As the water freezes into the hexagonal crystals of ice, these hydrogen bonds are forced farther apart and the volume increases. With this volume increase comes a decrease in density. This explains why ice floats to the top of a cup of water: the ice is less dense.

Even though the rule of density and temperature has its exceptions, it is still useful. For example, it explains how hot air balloons work.



Density and Pressure

Density increases with increasing pressure because volume decreases as pressure increases. And since density=mass/volume , the lower the volume, the higher the density. This is why all density values in the Periodic Table are recorded at STP, as mentioned in the section "Density and the Periodic Table." The decrease in volume as related to pressure is explained in Boyle's Law: $P_1V_1 = P_2V_2$ where P = pressure and V = volume. This idea is explained in the figure below.



Archimedes' Principle

The Greek scientist Archimedes made a significant discovery in 212 B.C. The story goes that Archimedes was asked to find out for the King if his goldsmith was cheating him by replacing his gold for the crown with silver, a cheaper metal. Archimedes did not know how to find the volume of an irregularly shaped object such as the crown, even though he knew he could distinguish between elements by their density. While meditating on this puzzle in a bath, Archimedes recognized that when he entered the bath, the water rose. He then realized that he could use a similar process to determine the density of the crown! He then supposedly ran

through the streets naked shouting "Eureka," which means "I found it!" in Latin.

Archimedes then tested the king's crown by taking a genuine gold crown of equal mass and comparing the densities of the two. The king's crown displaced more water than the gold crown of the same mass, meaning that the king's crown had a greater volume and thus had a smaller density than the real gold crown. The king's "gold" crown, therefore, was not made of pure gold. Of course, this tale is disputed today because Archimedes was not precise in all his measurements, which would make it hard to determine accurately the differences between the two crowns.

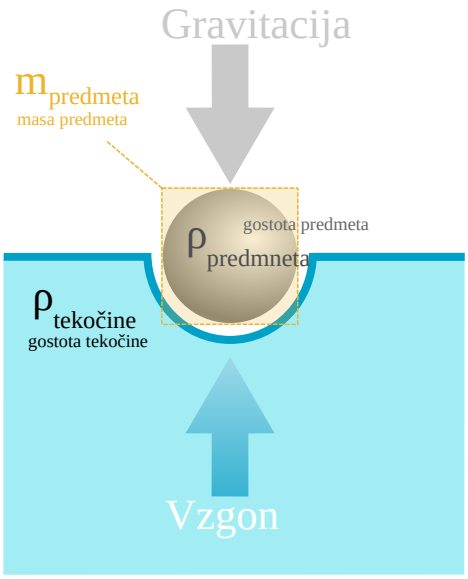


Figure 1.5.2: The forces at work in buoyancy. Note that the object is floating because the upward force of buoyancy is equal to the downward force of gravity. (CC BY-SA 3.0; Yupi666 via Wikipedia.

Archimedes' Principle states that if an object has a greater density than the liquid that it is placed into, it will sink and displace a volume of liquid equal to its own. If it has a smaller density, it will float and displace a mass of liquid equal to its own. If the density is equal, it will not sink or float (Figure 1.5.2). The principle explains why balloons filled with helium float. Balloons, as we learned in the section concerning density and temperature, float because they are less dense than the surrounding air. Helium is less dense than the atmospheric air, so it rises. Archimedes' Principle can also be used to explain why boats float. Boats, including all the air space, within their hulls, are far less dense than water. Boats made of steel can float because they displace their mass in water without submerging all the way. The table below gives the densities of a few liquids to put things into perspective.

Table 1.5.3: Density of Common Liquids

Liquid	Density in kg/m^3	Density in g/cm^3
2-Methoxyethanol	964.60	0.9646
Acetic Acid	1049.10	1.049
Acetone	789.86	0.7898
Alcohol, ethyl	785.06	0.7851
Alcohol, methyl	786.51	0.7865
Ammonia	823.35	0.8234
Benzene	873.81	0.8738
Water, pure	1000.00	1.000

Percent Composition

Percent composition is very simple. **Percent composition** tells you by mass what percent of each element is present in a compound. A chemical compound is the combination of two or more elements. If you are studying a chemical compound, you may

want to find the percent composition of a certain element within that chemical compound. The equation for percent composition is

$$\text{Percent Composition} = \frac{\text{Total mass of element present}}{\text{Molecular mass}} \times 100\% \tag{1.5.4}$$

If you want to know the percent composition of the elements in an compound, follow these steps:

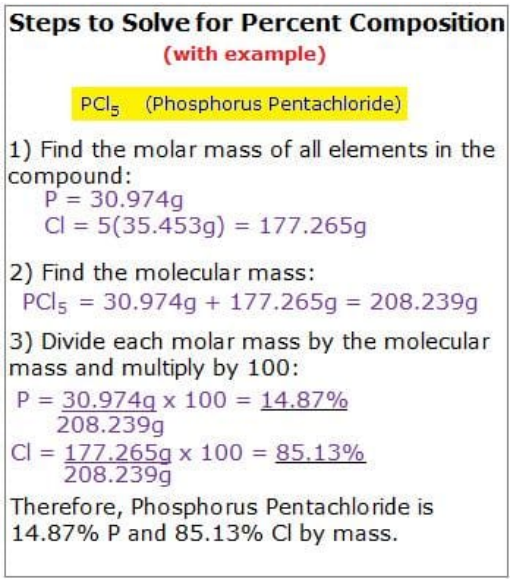
Steps to Solve:

1. Find the molar mass of all the elements in the compound in grams per mole.
2. Find the molecular mass of the entire compound.
3. Divide the component's molar mass by the entire molecular mass.
4. You will now have a number between 0 and 1. Multiply it by 100 to get percent composition!

Tips for solving:

1. The compounds will always add up to 100%, so in a binary compound, you can find the % of the first element, then do 100%-(% first element) to get (% second element)
2. If using a calculator, you can store the overall molar mass to a variable such as "A". This will speed up calculations, and reduce typographical errors.

These steps are outlined in the figure below.



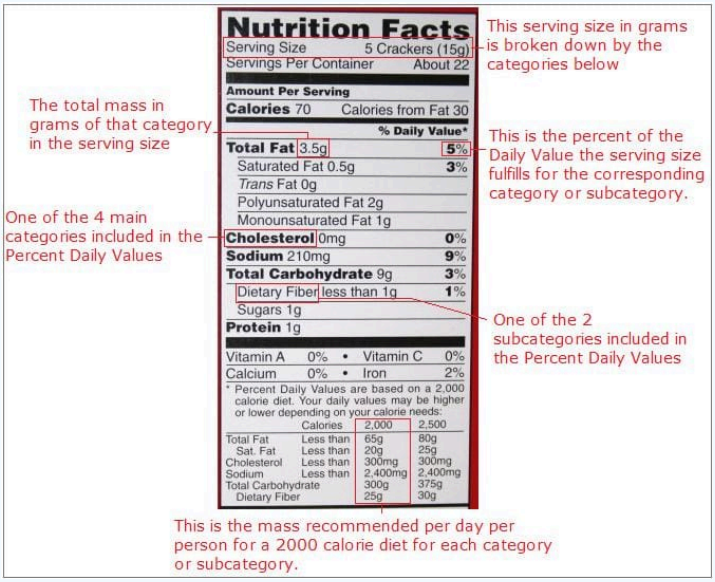
For another example, if you wanted to know the percent composition of hydrochloric acid (HCl), first find the molar mass of Hydrogen. H = 1.00794g. Now find the molecular mass of HCl: 1.00794g + 35.4527g = 36.46064g. Follow steps 3 and 4: (1.00794g/36.46064g) x 100 = 2.76% Now just subtract to find the percent by mass of Chlorine in the compound: 100%-2.76% = 97.24% Therefore, HCl is 2.76% Hydrogen and 97.24% Chlorine by mass.

Percent Composition in Everyday Life

Percent composition plays an important role in everyday life. It is more than just the amount of chlorine in your swimming pool because it concerns everything from the money in your pocket to your health and how you live. The next two sections describe percent composition as it relates to you.

Example 1.5.1: Nutritional Labels

The nutrition label found on the container of every bit of processed food sold by the local grocery store employs the idea of percent composition. On all nutrition labels, a known serving size is broken down in five categories: Total Fat, Cholesterol, Sodium, Total Carbohydrate, and Protein. These categories are broken down into further subcategories, including Saturated Fat and Dietary Fiber. The mass for each category, except Protein, is then converted to percent of Daily Value. Only two subcategories, Saturated Fat and Dietary Fiber are converted to percent of Daily Value. The Daily Value is based on a the mass of each category recommended per day per person for a 2000 calorie diet. The mass of protein is not converted to percent because their is no recommended daily value for protein. Following is a picture outlining these ideas.



For example, if you wanted to know the percent by mass of the daily value for sodium you are eating when you eat one serving of the food with this nutrition label, then go to the category marked sodium. Look across the same row and read the percent written. If you eat one serving of this food, then you will have consumed about 9% of your daily recommended value for sodium. To find the percent mass of fat in the whole food, you could divide 3.5 grams by 15 grams, and see that this snack is 23.33% fat.

Example 1.5.2: The Lucky Penny

The penny should be called "the lucky copper *coated* coin." The penny has not been made of solid copper since part of 1857. After 1857, the US government started adding other cheaper metals to the mix. The penny, being only one cent, is literally not worth its weight in copper. People could melt copper pennies and sell the copper for more than the pennies were worth. After 1857, nickel was mixed with the more expensive copper. After 1864, the penny was made of bronze. Bronze is 95% copper and 5% zinc and tin. For one year, 1943, the penny had no copper in it due to the expense of the World War II. It was just zinc coated steel. After 1943 until 1982, the penny went through periods where it was brass or bronze.



Figure 1.5.3: Today, the penny in America is 2.5% copper with 97.5% zinc. The copper coats the outside of the penny while the inner portion is zinc. For comparison's sake, the penny in Canada is 94% steel, 1.5% nickel, and 4.5% copper.

The percent composition of a penny may actually affect health, particularly the health of small children and pets. Since the newer pennies are made mainly of zinc instead of copper, they are a danger to a child's health if ingested. Zinc is very susceptible to acid. If the thin copper coating is scratched and the hydrochloric acid present in the stomach comes into contact with the zinc core it could cause ulcers, anemia, kidney and liver damage, or even death in severe cases. Three important factors in penny ingestion are time, pH of the stomach, and amount of pennies ingested. Of course, the more pennies swallowed, the more danger of an overdose of zinc. The more acidic the environment, the more zinc will be released in less time. This zinc is then absorbed and sent to the liver where it begins to cause damage. In this kind of situation, time is of the essence. The faster the penny is removed, the less zinc is absorbed. If the penny or pennies are not removed, organ failure and death can occur.

Below is a picture of a scratched penny before and after it had been submerged in lemon juice. Lemon juice has a similar pH of 1.5-2.5 when compared to the normal human stomach after food has been consumed. Time elapsed: 36 hours.





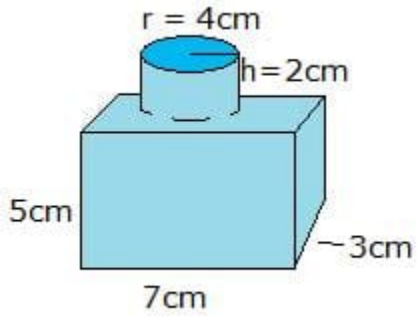
As you can see, the copper is vastly unharmed by the lemon juice. That's why pennies made before 1982 with mainly copper (except the 1943 penny) are relatively safe to swallow. Chances are they would pass through the digestive system naturally before any damage could be done. Yet, it is clear that the zinc was partially dissolved even though it was in the lemon juice for only a limited amount of time. Therefore, the percent composition of post 1982 pennies is hazardous to your health and the health of your pets if ingested.

Problems

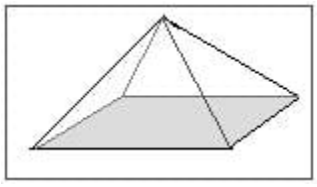
Following are examples of different types of percent composition and density problems.

Density Problems: These problems are meant to be easy in the beginning and then gradually become more challenging. Unless otherwise stated, answers should be in **g/mL** or the equivalent **g/cm^3**.

1. If you have a 2.130 mL sample of acetic acid with mass 0.002234 kg, what is the density?
2. Calculate the density of a .03020 L sample of ethyl alcohol with a mass of 23.71002 g.
3. Find the density of a sample that has a volume of 36.5 L and a mass of 10.0 kg.
4. Find the volume in mL of an object that has a density of 10.2 g/L and a mass of 30.0 kg.
5. Calculate the mass in grams of an object with a volume of 23.5 mL and density of 10.0 g/L.
6. Calculate the density of a rectangular prism made of metal. The dimensions of the prism are: 5 cm by 4 cm by 5 cm. The metal has a mass of 50 grams.
7. Find the density of an unknown liquid in a beaker. The beaker's mass is 165 g when there is no liquid present. With the unknown liquid, the total mass is 309 g. The volume of the unknown is 125 mL.
8. Determine the density in g/L of an unknown with the following information. A 55 gallon tub weighs 137.5lb when empty and 500.0 lb when filled with the unknown.
9. A ring has a mass of 5.00g and a volume of 0.476 mL. Is it pure silver?
10. What is the density of the solid in the image if the mass is 40 g? Make your answer have 3 significant figures.



11. Below is a model of a pyramid found at an archeological dig made of an unknown substance. It is too large to find the volume by submerging it in water. Also, the scientists refuse to remove a piece to test because this pyramid is a part of history. Its height is 150.0m. The length of its base is 75.0m and the width is 50.0m. The mass of this pyramid is 5.50x10^{5}kg. What is the density?



Percent Composition Problems: These problems will follow the same pattern of difficulty as those of density.

12. Calculate the percent by mass of each element in Cesium Fluoride (CsF).
13. Calculate the percent by mass of each element present in carbon tetrachloride (CCl_4)
14. A solution of salt and water is 33.0% salt by mass and has a density of 1.50 g/mL. What mass of the salt in grams is in 5.00L

of this solution?

15. A solution of water and HCl contains 25% HCl by mass. The density of the solution is 1.05 g/mL. If you need 1.7g of HCl for a reaction, what volume of this solution will you use?
16. A solution containing 42% NaOH by mass has a density of 1.30 g/mL. What mass, in kilograms, of NaOH is in 6.00 L of this solution?

Answers

Here are the solutions to the listed practice problems.

Density Problem Solutions

1. 1.049 g/mL
2. 0.7851 g/mL
3. 0.274 g/mL
4. 2.94 x 10^6 mL
5. 0.3.27 kg
6. 0.5 g/cm^3
7. 1.15 g/mL
8. 790 g/L
9. Yes
10. 0.195 g/cm^3
11. 29.3 g/cm^3

Percent Composition Problem Solutions

12. CsF is 87.5% Cs and 12.5% F by mass
13. CCl_4 is 92.2% Cl and 7.8% C by mass
14. 2480 g
15. 6.5 mL
16. 3.26 kg

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1.6: Uncertainties in Scientific Measurements

Learning Objectives

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

All measurements have a degree of uncertainty regardless of precision and accuracy. This is caused by two factors, the limitation of the measuring instrument (systematic error) and the skill of the experimenter making the measurements (random error).

Introduction

The graduated buret in Figure 1.6.1 contains a certain amount of water (with yellow dye) to be measured. The amount of water is somewhere between 19 ml and 20 ml according to the marked lines. By checking to see where the bottom of the meniscus lies, referencing the ten smaller lines, the amount of water lies between 19.8 ml and 20 ml. The next step is to estimate the uncertainty between 19.8 ml and 20 ml. Making an approximate guess, the level is less than 20 ml, but greater than 19.8 ml. We then report that the measured amount is approximately 19.9 ml. The graduated cylinder itself may be distorted such that the graduation marks contain inaccuracies providing readings slightly different from the actual volume of liquid present.



Figure 1.6.1: A meniscus as seen in a burette of colored water. '20.00 mL' is the correct depth measurement.

Systematic vs. Random Error

Systematic errors: When we use tools meant for measurement, we assume that they are correct and accurate, however measuring tools are not always right. In fact, they have errors that naturally occur called **systematic errors**. Systematic errors tend to be consistent in magnitude and/or direction. If the magnitude and direction of the error is known, accuracy can be improved by additive or proportional corrections. **Additive correction** involves adding or subtracting a constant adjustment factor to each measurement; **proportional correction** involves multiplying the measurement(s) by a constant.

Random errors: Sometimes called human error, random error is determined by the experimenter's skill or ability to perform the experiment and read scientific measurements. These errors are random since the results yielded may be too high or low. Often random error determines the precision of the experiment or limits the precision. For example, if we were to time a revolution of a steadily rotating turnable, the random error would be the reaction time. Our reaction time would vary due to a delay in starting (an underestimate of the actual result) or a delay in stopping (an overestimate of the actual result). Unlike systematic errors, random errors vary in magnitude and direction. It is possible to calculate the average of a set of measured positions, however, and that average is likely to be more accurate than most of the measurements.

Accuracy and Precision

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. Figure 1.6.1 help to understand the difference between precision (small expected difference between multiple measurements) and accuracy (difference between the result and a known value).

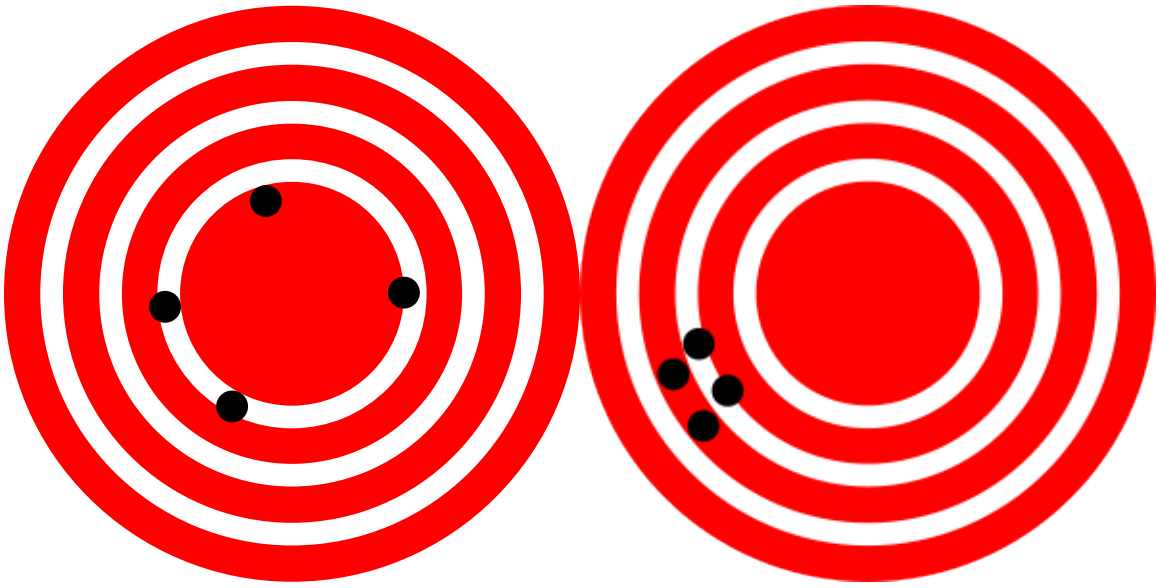


Figure 1.6.1: (left) Random error are characterized by high accuracy and low Precision (right) Systematic errors are characterized by high precision but low accuracy. (Public Domain; DarkEvil)

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:

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:

$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}} \tag{1.6.1}$$

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

$$deviation = |\text{measurement} - \text{average}| \tag{1.6.2}$$

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:

$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}} \tag{1.6.3}$$

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

$$\frac{1.125\ g + 1.158\ g + 1.067\ g}{3} = 1.117\ g \tag{1.6.4}$$

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

$$\frac{0.008\ g + 0.041\ g + 0.050\ g}{3} = 0.033\ g \tag{1.6.5}$$

The precision of this set of measurements is therefore

$$\frac{0.033\ g}{1.117\ g} \times 100 = 3.0\% \tag{1.6.6}$$

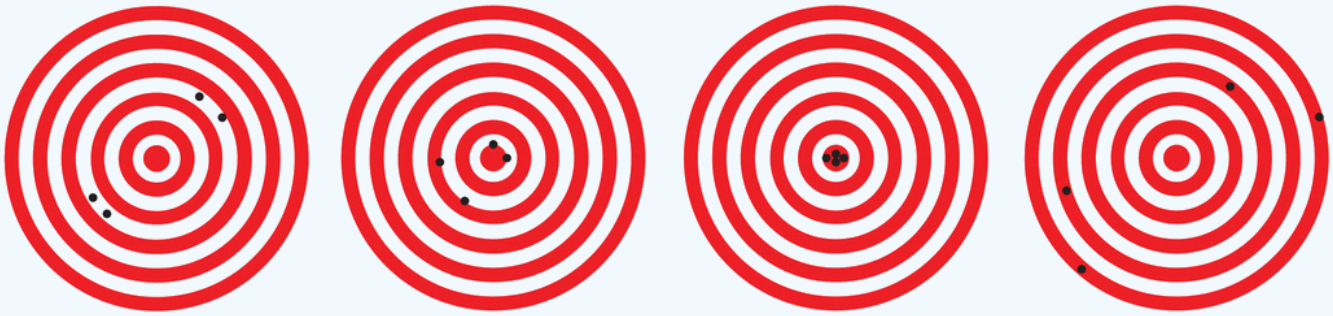
When a series of measurements is precise but not accurate, the error is usually systematic. Systematic errors can be caused by faulty instrumentation or faulty technique.

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 1.6.1

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?



Solution

a. (B)
b. (a)

c. (c)
d. (d)

Example 1.6.2

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 (1) the limitations of instruments and measuring devices (such as the size of the divisions on a graduated cylinder) and (2) the imperfection of human senses. 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.

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:

$$1 ft = 12 in$$

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 1.6.3

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

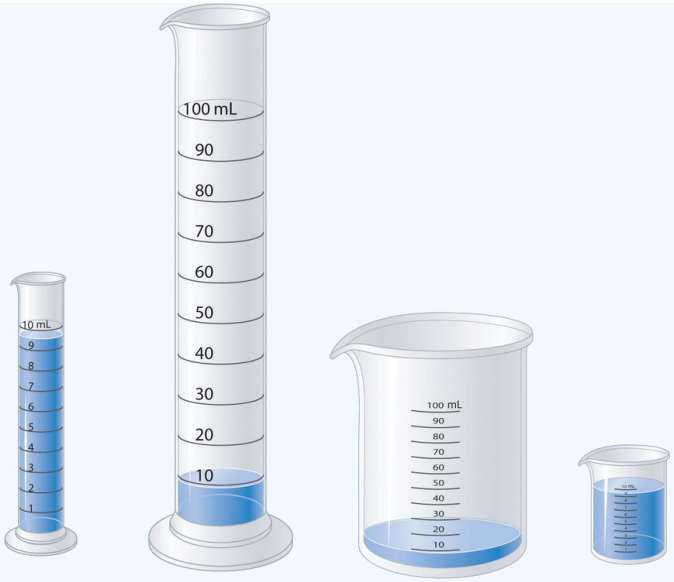
a. 5.87
b. 0.031
c. 52.90
d. 00.2001
e. 500
f. 6 atoms

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 1.6.4

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?



Solution

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

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 + 21.2	36
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 × 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.

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.

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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Significant Figures: https://youtu.be/E-OAkZglfO8

Problems

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

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1.7: Significant Figures

Learning Objectives

- Give an example of a measurement whose number of significant digits is clearly too great, and explain why.
- State the purpose of rounding off, and describe the information that must be known to do it properly.
- Round off a number to a specified number of significant digits.
- Explain how to round off a number whose second-most-significant digit is 9.
- Carry out a simple calculation that involves two or more observed quantities, and express the result in the appropriate number of significant figures.

The numerical values we deal with in science (and in many other aspects of life) represent measurements whose values are never known exactly. Our pocket-calculators or computers don't know this; they treat the numbers we punch into them as "pure" mathematical entities, with the result that the operations of arithmetic frequently yield answers that are physically ridiculous even though mathematically correct. The purpose of this unit is to help you understand why this happens, and to show you what to do about it.

Digits: Significant and otherwise

Consider the two statements shown below:

- **"The population of our city is 157,872."**
- **"The number of registered voters as of Jan 1 was 27,833.**

Which of these would you be justified in dismissing immediately? Certainly not the second one, because it probably comes from a database which contains one record for each voter, so the number is found simply by counting the number of records. The first statement cannot possibly be correct. Even if a city's population could be defined in a precise way (Permanent residents? Warm bodies?), how can we account for the minute-by minute changes that occur as people are born and die, or move in and move away?

What is the difference between the two population numbers stated above? The first one expresses a quantity that cannot be known exactly — that is, it carries with it a degree of uncertainty. It is quite possible that the last census yielded precisely 157,872 records, and that this might be the "population of the city" for legal purposes, but it is surely not the "true" population. To better reflect this fact, one might list the population (in an atlas, for example) as **157,900** or even **158,000**. These two quantities have been rounded off to four and three significant figures, respectively, and the have the following meanings:

- **157900** (the significant digits are underlined here) implies that the population is believed to be within the range of about 157850 to about 157950. In other words, the population is 157900±50. The "plus-or-minus 50" appended to this number means that we consider the absolute uncertainty of the population measurement to be 50 – (–50) = 100. We can also say that the relative uncertainty is 100/157900, which we can also express as 1 part in 1579, or 1/1579 = 0.000633, or about 0.06 percent.
- The value **158000** implies that the population is likely between about 157500 and 158500, or 158000±500. The absolute uncertainty of 1000 translates into a relative uncertainty of 1000/158000 or 1 part in 158, or about 0.6 percent.

Which of these two values we would report as "the population" will depend on the degree of confidence we have in the original census figure; if the census was completed last week, we might round to four significant digits, but if it was a year or so ago, rounding to three places might be a more prudent choice. In a case such as this, there is no really objective way of choosing between the two alternatives.

This illustrates an important point: the concept of *significant digits* has less to do with mathematics than with our confidence in a measurement. This confidence can often be expressed numerically (for example, the height of a liquid in a measuring tube can be read to ±0.05 cm), but when it cannot, as in our population example, we must depend on our personal experience and judgment.

So, what is a significant digit? According to the usual definition, it is all the numerals in a measured quantity (counting from the

left) whose values are considered as known exactly, plus one more whose value could be one more or one less:

- In “157900” (four significant digits), the left most three digits are known exactly, but the fourth digit, “9” could well be “8” if the “true value” is within the implied range of 157850 to 157950.
- In “*158*000” (three significant digits), the left most two digits are known exactly, while the third digit could be either “7” or “8” if the true value is within the implied range of 157500 to 158500.



Although rounding off always leads to the loss of numeric information, what we are getting rid of can be considered to be “numeric noise” that does not contribute to the quality of the measurement. The purpose in rounding off is to avoid expressing a value to a greater degree of precision than is consistent with the uncertainty in the measurement.

Implied Uncertainty

If you know that a balance is accurate to within 0.1 mg, say, then the uncertainty in any measurement of mass carried out on this balance will be ±0.1 mg. Suppose, however, that you are simply told that an object has a length of 0.42 cm, with no indication of its precision. In this case, all you have to go on is the number of digits contained in the data. Thus the quantity “0.42 cm” is specified to 0.01 unit in 0 42, or one part in 42 . The implied relative uncertainty in this figure is 1/42, or about 2%. The precision of any numeric answer calculated from this value is therefore limited to about the same amount.

Rounding Error

It is important to understand that the number of significant digits in a value provides only a rough indication of its precision, and that information is lost when rounding off occurs. Suppose, for example, that we measure the weight of an object as 3.28 g on a balance believed to be accurate to within ±0.05 gram. The resulting value of 3.28±.05 gram tells us that the true weight of the object could be anywhere between 3.23 g and 3.33 g. The absolute uncertainty here is 0.1 g (±0.05 g), and the relative uncertainty is 1 part in 32.8, or about 3 percent.

How many significant digits should there be in the reported measurement? Since only the left most “3” in “3.28” is certain, you would probably elect to round the value to 3.3 g. So far, so good. But what is someone else supposed to make of this figure when they see it in your report? The value “3.3 g” suggests an *implied uncertainty* of 3.3±0.05 g, meaning that the true value is likely between 3.25 g and 3.35 g. This range is 0.02 g below that associated with the original measurement, and so rounding off has introduced a bias of this amount into the result. Since this is less than half of the ±0.05 g uncertainty in the weighing, it is not a very serious matter in itself. However, if several values that were rounded in this way are combined in a calculation, the rounding-off errors could become significant.

Rules for Rounding

The standard rules for rounding off are well known. Before we set them out, let us agree on what to call the various components of a numeric value.

- The *most significant digit* is the left most digit (not counting any leading zeros which function only as placeholders and are

never significant digits.)
- If you are rounding off to ***n*** significant digits, then the *least significant digit* is the ***n***th digit from the most significant digit. The least significant digit can be a zero.
- The first non-significant digit is the ***n***+1th digit.

Rounding-off rules

- If the first non-significant digit is less than 5, then the least significant digit remains unchanged.
- If the first non-significant digit is greater than 5, the least significant digit is incremented by 1.
- If the first non-significant digit is 5, the least significant digit can either be incremented or left unchanged (*see below!*)
- All non-significant digits are removed.

Fantasies about fives

Students are sometimes told to increment the least significant digit by 1 if it is odd, and to leave it unchanged if it is even. One wonders if this reflects some idea that even numbers are somehow “better” than odd ones! (The ancient superstition is just the opposite, that only the odd numbers are "lucky".)

In fact, you could do it equally the other way around, incrementing only the even numbers. If you are only rounding a single number, it doesn't really matter what you do. However, when you are rounding a series of numbers that will be used in a calculation, if you treated each first nonsignificant 5 in the same way, you would be over- or understating the value of the rounded number, thus accumulating round-off error. Since there are equal numbers of even and odd digits, incrementing only the one kind will keep this kind of error from building up. You could do just as well, of course, by flipping a coin!

Table 1.7.1*: Examples of rounding-off*

number to round	number of significant digits	result	comment
34.216	3	34.2	First non-significant digit (1) is less than 5, so number is simply truncated.
2.252	2	2.2 or 2.3	First non-significant digit is 5, so least sig. digit can either remain unchanged or be incremented.
39.99	3	40.0	Crossing "decimal boundary", so all numbers change.
85,381	3	85,400	The two zeros are just placeholders
0.04597	3	0.0460	The two leading zeros are not significant digits.

Rounding up the Nines

Suppose that an object is found to have a weight of 3.98 ± 0.05 g. This would place its true weight somewhere in the range of **3.93** g to **4.03** g. In judging how to round this number, you count the number of digits in “3.98” that are known exactly, and you find none! Since the “4” is the left most digit whose value is uncertain, this would imply that the result should be rounded to one significant figure and reported simply as 4 g. An alternative would be to bend the rule and round off to two significant digits, yielding 4.0 g. How can you decide what to do? In a case such as this, you should look at the implied uncertainties in the two values, and compare them with the uncertainty associated with the original measurement.

Table 1.7.2

rounded value	implied max	implied min	absolute uncertainty	relative uncertainty
3.98 g	3.985 g	3.975 g	±.005 g or 0.01 g	1 in 400, or 0.25%
4 g	4.5 g	3.5 g	±.5 g or 1 g	1 in 4, 25%
4.0 g	**4.05 g**	**3.95 g**	**±.05 g or 0.1 g**	**1 in 40, 2.5%**

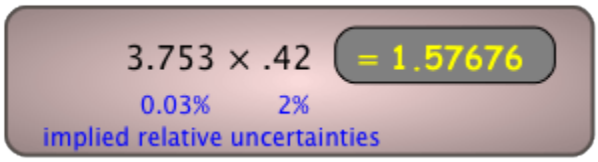
Clearly, rounding off to two digits is the only reasonable course in this example. Observed values should be rounded off to the

number of digits that most accurately conveys the uncertainty in the measurement.

- Usually, this means rounding off to the number of significant digits in in the quantity; that is, the number of digits (counting from the left) that are known exactly, plus one more.
- When this cannot be applied (as in the example above when addition of subtraction of the absolute uncertainty bridges a power of ten), then we round in such a way that the relative implied uncertainty in the result is as close as possible to that of the observed value.

Rounding the Results of Calculations

When carrying out calculations that involve multiple steps, you should avoid doing any rounding until you obtain the final result. Suppose you use your calculator to work out the area of a rectangle:



rounded value	relative implied uncertainty
1.58	1 part in 158, or 0.6%
1.6	1 part in 16, or 6 %

Note

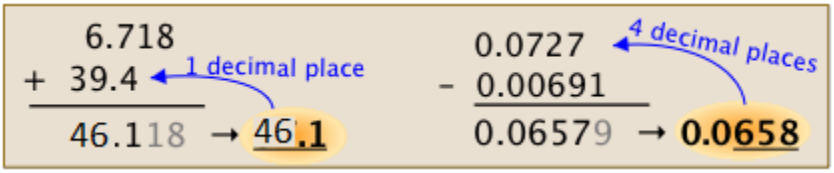
Your calculator is of course correct as far as the pure numbers go, but you would be wrong to write down "1.57676 cm^2" as the answer. Two possible options for rounding off the calculator answer are shown at the right.

It is clear that neither option is entirely satisfactory; rounding to 3 significant digits overstates the precision of the answer, whereas following the rule and rounding to the two digits in ".42" has the effect of throwing away some precision. In this case, it could be argued that rounding to three digits is justified because the implied relative uncertainty in the answer, 0.6%, is more consistent with those of the two factors.

> The "rules" for rounding off are generally useful, convenient guidelines, but they do not always yield the most desirable result. When in doubt, it is better to rely on relative implied uncertainties.

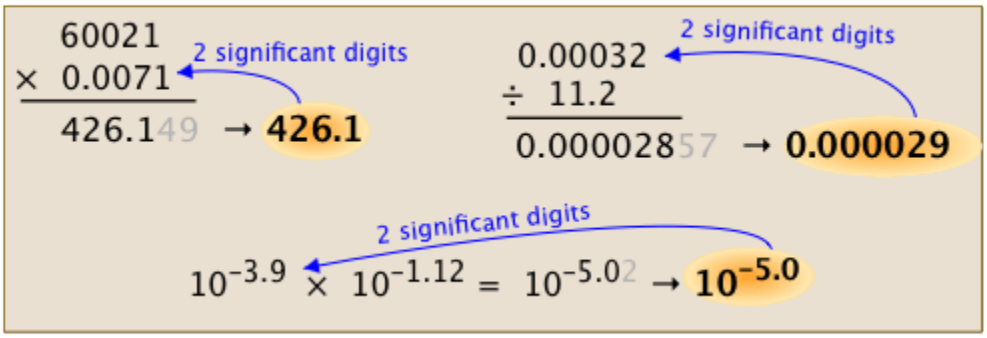
Addition and Subtraction

In operations involving significant figures, the answer is reported in such a way that it reflects the reliability of the **least precise** operation. An answer is no more precise that the least precise number used to get the answer. When adding or subtracting, we go by the number of *decimal places* (i.e., the number of digits on the right side of the decimal point) rather than by the number of significant digits. Identify the quantity having the smallest number of decimal places, and use this number to set the number of decimal places in the answer.



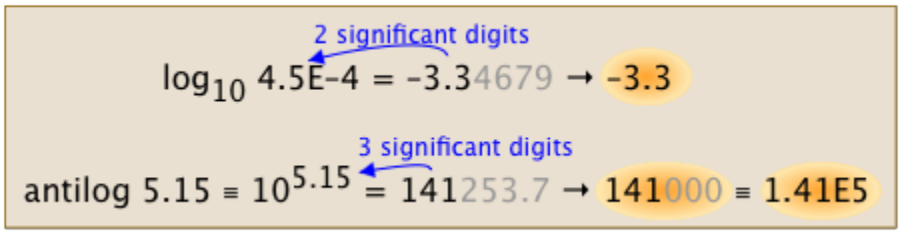
Multiplication and Division

The result must contain the same number of significant figures as in the value having the least number of significant figures.



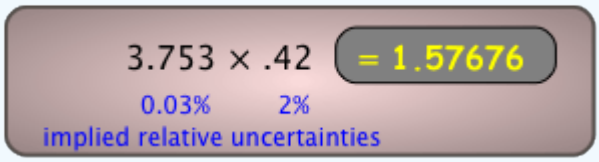
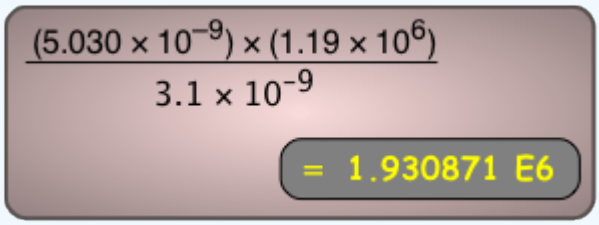
Logarithms and antilogarithms

If a number is expressed in the form $a \times 10^b$ ("scientific notation") with the additional restriction that the coefficient a is no less than 1 and less than 10, the number is in its *normalized* form. Express the base-10 logarithm of a value using the same number of significant figures as is present in the *normalized form* of that value. Similarly, for antilogarithms (numbers expressed as powers of 10), use the same number of significant figures as are in that power.



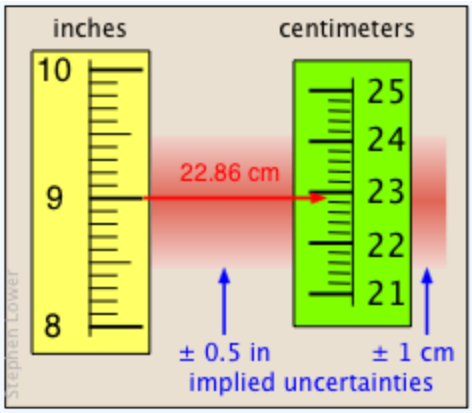
Examples 1.7.1

The following examples will illustrate the most common problems you are likely to encounter in rounding off the results of calculations. They deserve your careful study!

calculator result	rounded	remarks
	1.6	Rounding t two significant figures yields an implied uncertainty of 1/16 or 6%, three times greater than that ir the least-precisely known factor. This is a good illustration of how rounding can lead to the loss of informatior
	1.9E6	The "3.1" factor is specified t 1 part in 31 or 3%. In the answer 1.9, the value is expressed to 1 part in 19, or 5%. These precisions are comparable so the rounding-off rule has given us a reasonable result.

A certain book has a thickness of 117 mm; find the height of a stack of 24 identical books: $(24\ \text{books}) \times \frac{(117\ \text{cm})}{(1\ \text{book})} = 2808\ \text{cm}$	2810 mm	The “24” and the “1” are exact, so the only uncertain value is the thickness o each book, given to 3 significant digits. The trailing zer in the answer is only a placeholde
$7.01 + 0.0007 + 3.4 = 10.4107$	10.4	In addition or subtraction look for the term having the smalles number of decimal places, and round off the answer to the same number of places.
$(9\ \text{in}) \times \frac{(2.54\ \text{cm})}{(1\ \text{in})} = 22.86\ \text{cm}$		
	23 cm	see below

The last of the examples shown above represents the very common operation of converting one unit into another. There is a certain amount of ambiguity here; if we take "9 in" to mean a distance in the range 8.5 to 9.5 inches, then the implied uncertainty is ±0.5 in, which is 1 part in 18, or about ± 6%. The relative uncertainty in the answer must be the same, since all the values are multiplied by the same factor, 2.54 cm/in. In this case we are justified in writing the answer to two significant digits, yielding an uncertainty of about ±1 cm; if we had used the answer "20 cm" (one significant digit), its implied uncertainty would be ±5 cm, or ±25%.



When the appropriate number of significant digits is in question, calculating the relative uncertainty can help you decide.

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1.E: Exercises

1.1: The Scientific Method

Problems

1. What are the three components of the scientific method? Is it necessary for an individual to conduct experiments to follow the scientific method?

2. Identify each statement as a theory or a law and explain your reasoning.

    a. The ratio of elements in a pure substance is constant.

    b. An object appears black because it absorbs all the visible light that strikes it.

    c. Energy is neither created nor destroyed.

    d. Metals conduct electricity because their electrons are not tightly bound to a particular nucleus and are therefore free to migrate.

3. Identify each statement as a theory or a law and explain your reasoning.

    a. A pure chemical substance contains the same proportion of elements by mass.

    b. The universe is expanding.

    c. Oppositely charged particles attract each other.

    d. Life exists on other planets.

4. Classify each statement as a qualitative observation or a quantitative observation.

    a. Mercury and bromine are the only elements that are liquids at room temperature.

    b. An element is both malleable and ductile.

    c. The density of iron is 7.87 g/cm3.

    d. Lead absorbs sound very effectively.

    e. A meteorite contains 20% nickel by mass.

5. Classify each statement as a quantitative observation or a qualitative observation.

    a. Nickel deficiency in rats is associated with retarded growth.

    b. Boron is a good conductor of electricity at high temperatures.

    c. There are 1.4–2.3 g of zinc in an average 70 kg adult.

    d. Certain osmium compounds found in air in concentrations as low as 10.7 µg/m3 can cause lung cancer.

Answers

3.

a. law

b. theory

c. law

d. theory

5.

a. qualitative

b. qualitative

c. quantitative

d. quantitative

1.2: Properties of Matter

1.3: Classification of Matter

1.4: Measurement of Matter: SI (Metric) Units

1.5: Density and Percent Composition: Their Use in Problem Solving

1.6: Uncertainties in Scientific Measurements

1.7: Significant Figures

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2: ATOMS AND THE ATOMIC THEORY

Petrucci: *General Chemistry*
Principles and Modern Applications

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Homework Problems

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2.1: Early Chemical Discoveries and the Atomic Theory

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 article explains the theories that Dalton used as a basis for his theory:

1. Law of Conservation of Mass
2. Law of Definite Proportions
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.

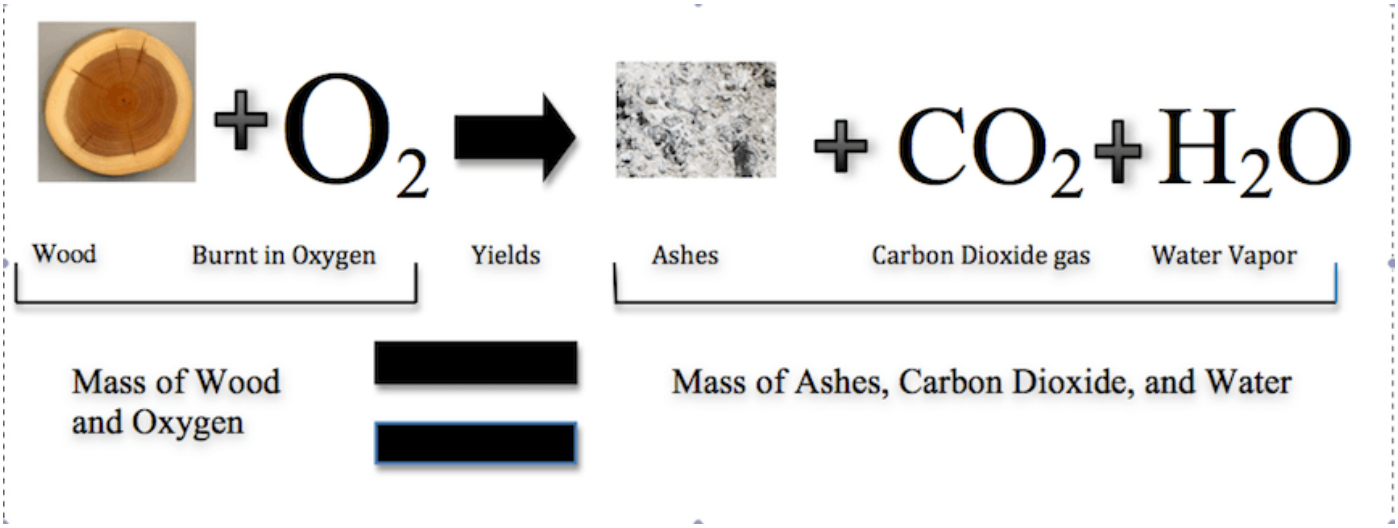
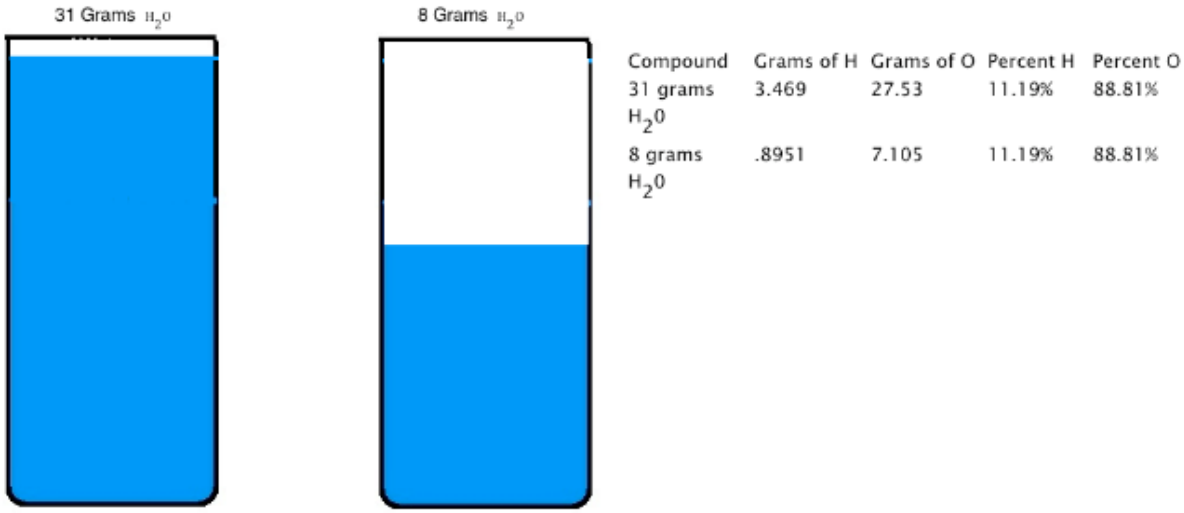


Figure 2.1.1: Image of the wood courtesy of Ehamberg and Stannered on Wikimedia Commons, available under Creative Commons Attribution 2.5 Generic license. Image of ashes courtesy of Walter Siegmund. Image as a whole constructed by Jessica Thornton (UCD).

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.

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; 31 grams of H_2O and 8 grams of H_2O are made up of the same percent of hydrogen and oxygen.



Compound	Grams of H	Grams of O	Percent H	Percent O
31 grams H_2O	3.469	27.53	11.19%	88.81%
8 grams H_2O	.8951	7.105	11.19%	88.81%

Figure 2.1.2: Constructed by Jessica Thornton (UCD)

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.

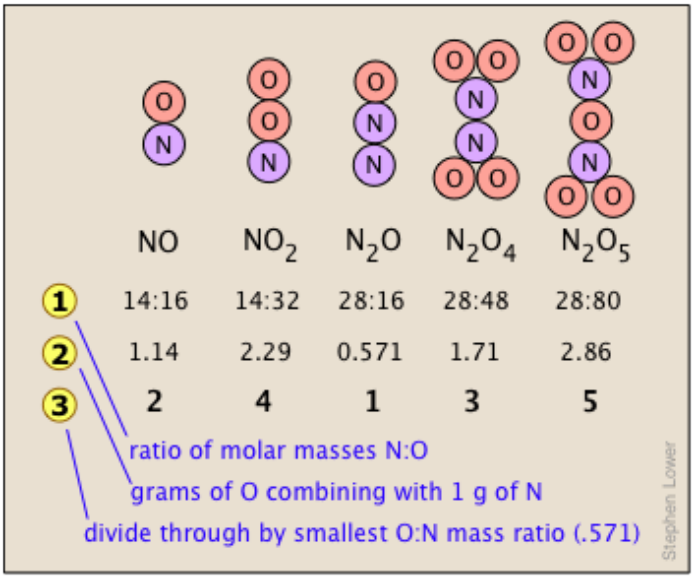


Figure 2.1.3: Law of Multiple Proportions applied to nitrogen oxides (NO_x) compounds.

- 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) = 13:32. (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 consistant 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:

$$\frac{0.571\ g\ oxygen}{0.429\ g\ carbon} = 1.33\ \frac{goxygen}{gcarbon} \tag{2.1.1}$$

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

$$\frac{0.727\ g\ oxygen}{0.273\ g\ carbon} = 2.66\ \frac{goxygen}{gcarbon} \tag{2.1.2}$$

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

$$\frac{2.66}{1.33} = 2 \tag{2.1.3}$$

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).

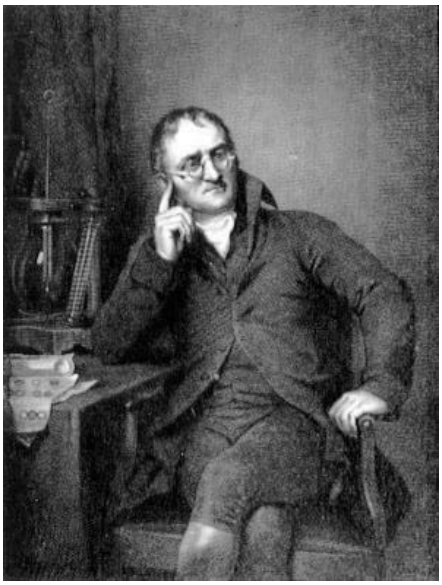


Figure 2.1.4 John Dalton was an English scientist who enunciated the modern atomic theory.

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. Consequentially, John Dalton is often considered to be the father of modern atomic theory.

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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Fundamental Experiments in Chemistry: https://youtu.be/IhqqLGKmah4

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Summary

This article explains the theories that Dalton used as a basis for his theory:

- Law of Conservation of Mass
- Law of Constant Composition
- Law of Multiple Proportions

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2.2: Electrons and Other Discoveries in Atomic Physics

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.

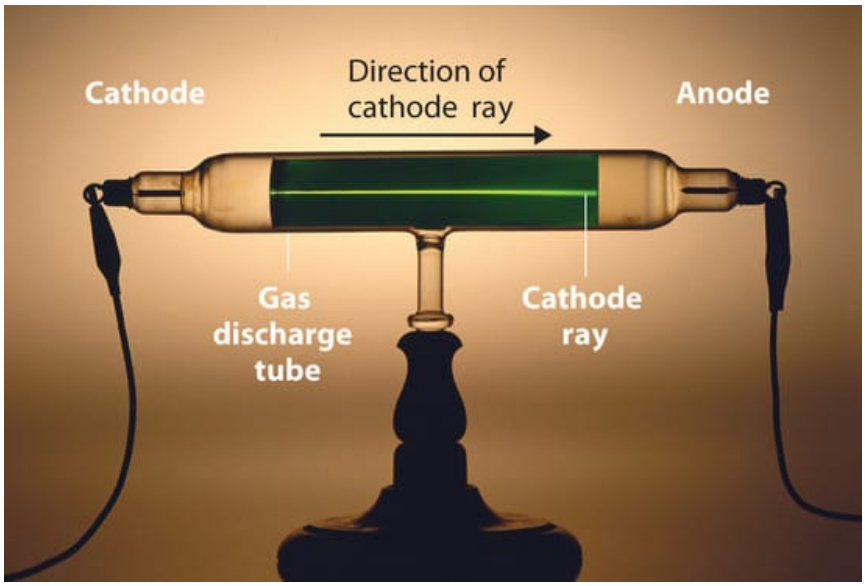


Figure 2.2.1: A Gas Discharge Tube Producing Cathode Rays. When a high voltage is applied to a gas contained at low pressure in a gas discharge tube, electricity flows through the gas, and energy is emitted in the form of light.

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.

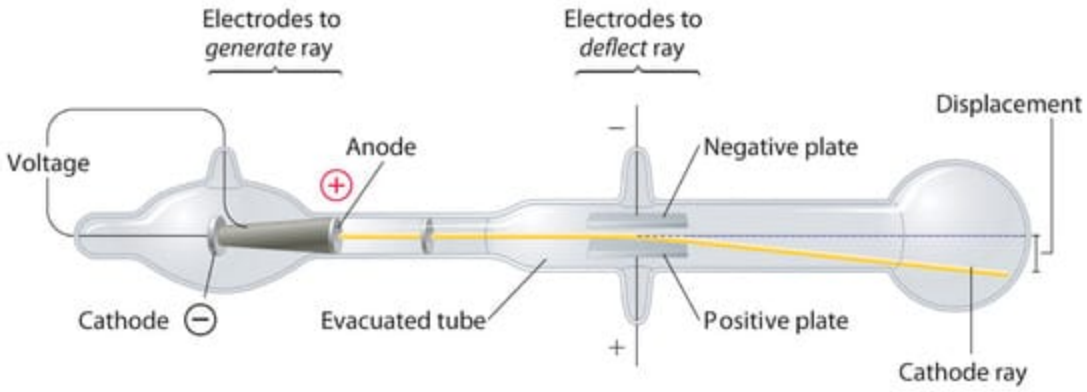


Figure 2.2.2: Deflection of Cathode Rays by an Electric Field. As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged.

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:

$$\frac{mass}{charge} \times charge = mass \tag{2.2.1}$$

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.

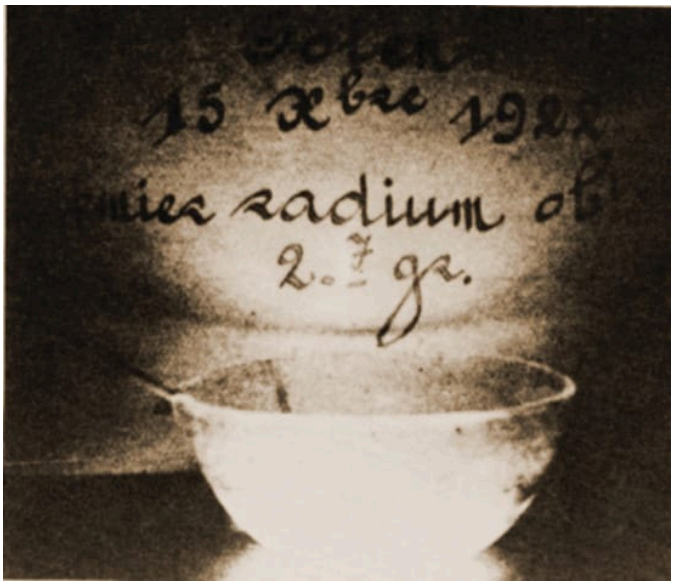


Figure 2.2.3: Radium bromide illuminated by its own radioactive glow. This 1922 photo was taken in the dark in the Curie laboratory.

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 a lower-energy form of radiation called x-rays, now used to produce images of bones and teeth.

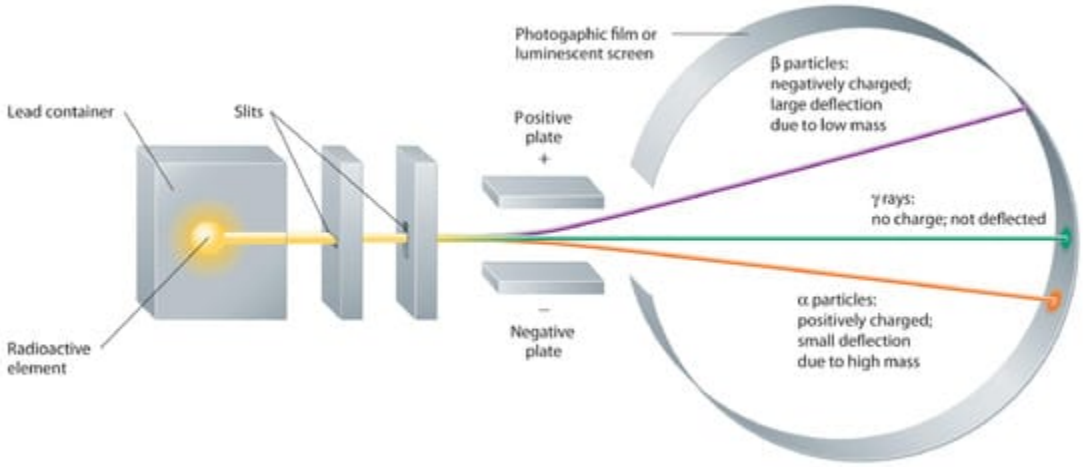


Figure 2.2.4: Effect of an Electric Field on α Particles, β Particles, and γ Rays. A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown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

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.

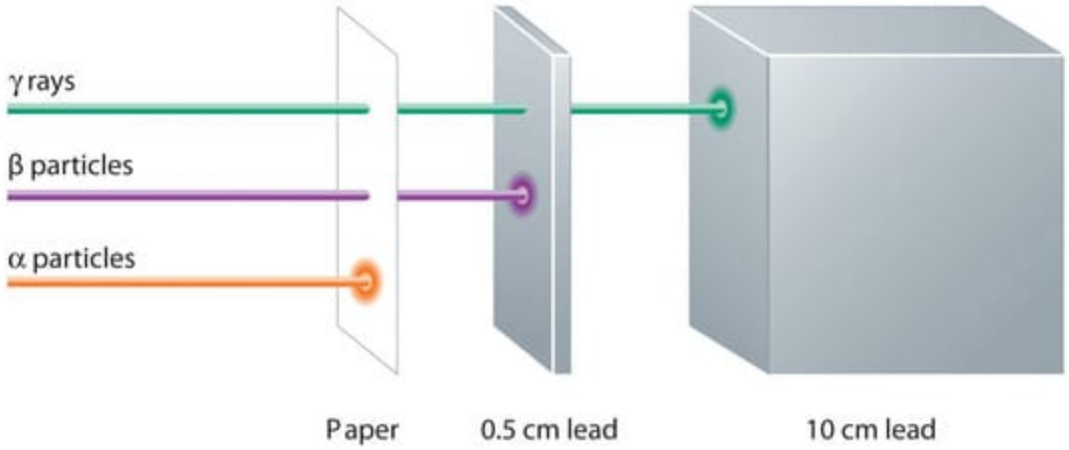


Figure 2.2.5: Relative Penetrating Power of the Three Types of Radiation. A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead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

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 Nuclear Atom

Learning Objectives

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

Dissecting the Atom

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 2.3.1).

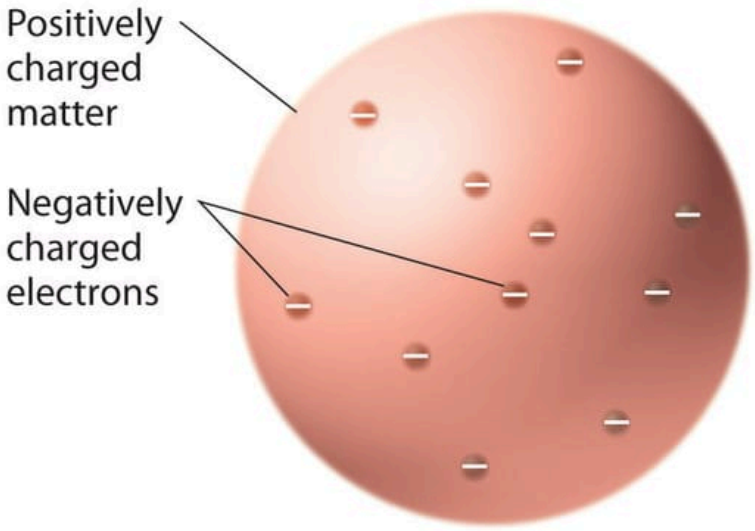


Figure 2.3.1: Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom. In this model, the electrons are embedded in a uniform sphere of positive charge.

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 (part (a) in Figure 2.3.2) 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 (part (b) in Figure 2.3.2). 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 (part (c) in Figure 2.3.2). 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."

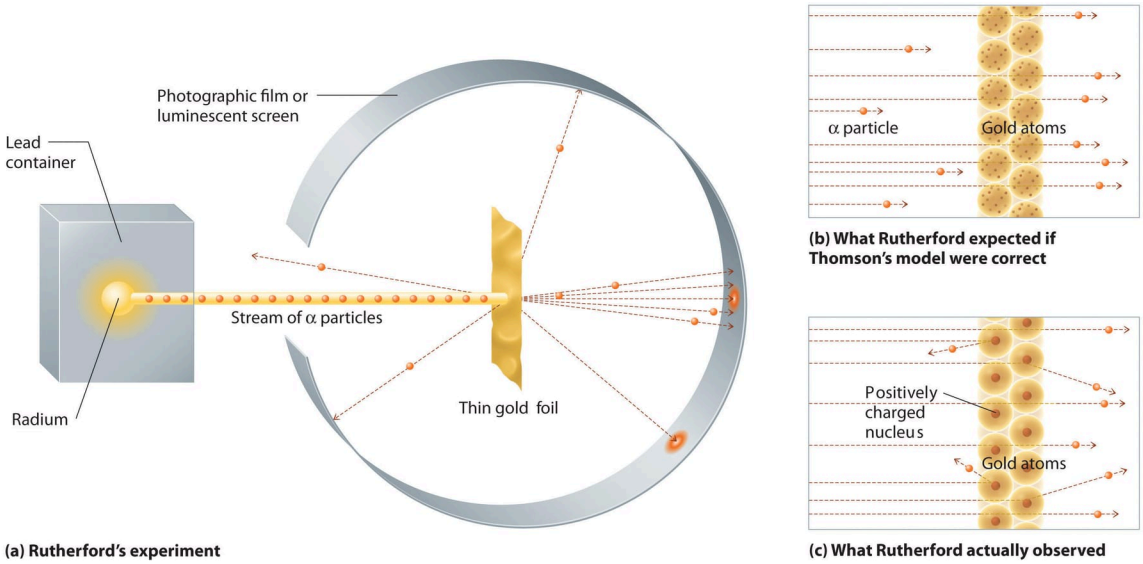


Figure 2.3.2: A Summary of Rutherford's Experiments. (a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles 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.

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."

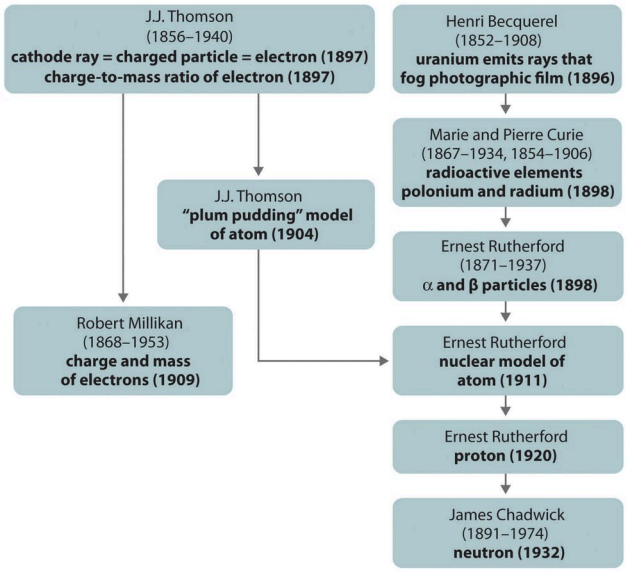


Figure 2.3.3: A Summary of the Historical Development of Models of the Components and Structure of the Atom. The dates in parentheses are the years in which the key experiments were performed.

The historical development of the different models of the atom's structure is summarized in Figure 2.3.3. 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.

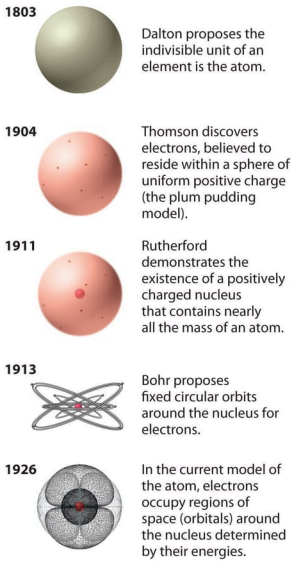


Figure 2.3.4: The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom. Bohr's model and the current model are described in Chapter 6, "The Structure of Atoms."

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

The Nuclear Atom

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.

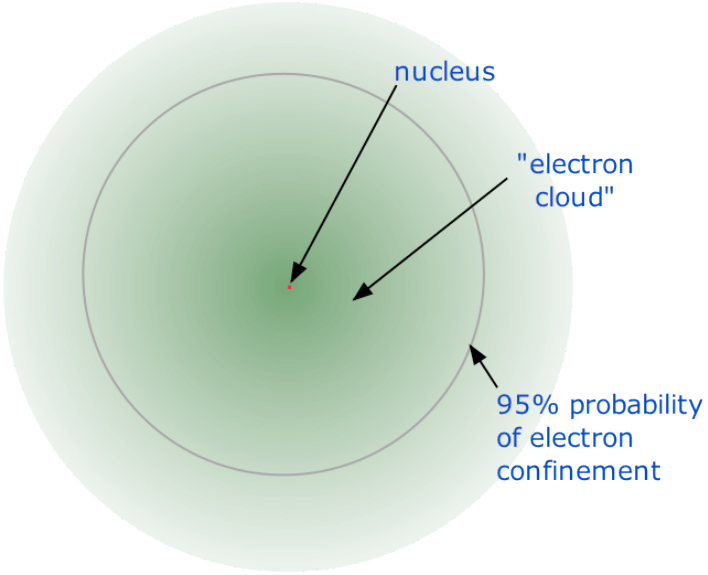


Figure 2.3.5: The structure of the nuclear atom with a central nucleus and surrounding electrons.

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.

Note

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*.

Atoms consist of electrons, protons, and neutrons. This is an oversimplification that ignores the other subatomic particles that have been discovered, but 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
neutron	1.675×10^{-24}	1.008665	0	0
proton	1.673×10^{-24}	1.007276	+1.602 × 10−19	+1
*** For a review of using scientific notation and units of measurement, see Essential Skills 1 (Section 1.9).**				

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The Nuclear Atom: https://youtu.be/eqoyZuv1tWA

Summary

- The atom consists of discrete particles that govern its chemical and physical behavior.

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).

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?

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. Using the data in Table 1.3 and the periodic table (see Chapter 32), 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 (see Chapter 32), 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?

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2.4: Chemical Elements

Learning Objectives

- To know the meaning of isotopes and atomic masses.

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. 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 2.4.1.

Table 2.4.1: 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

Atomic Number (Z)

What single parameter uniquely characterizes the atom of a given element? It is not the atom's relative mass, as we will see in the section on isotopes below. It is, rather, the number of protons in the nucleus, which we call the *atomic number* and denote by the symbol *Z*. Each proton carries an electric charge of +1, so the atomic number also specifies the electric charge of the nucleus. In the neutral atom, the *Z protons* within the nucleus are balanced by *Z electrons* outside it.

Henry Moseley

Atomic numbers were first worked out in 1913 by Henry Moseley, a young member of Rutherford's research group in Manchester. Moseley searched for a measurable property of each element that increases linearly with atomic number. He found this in a class of X-rays emitted by an element when it is bombarded with electrons. The frequencies of these X-rays

are unique to each element, and they increase uniformly in successive elements. Moseley found that the square roots of these frequencies give a straight line when plotted against Z; this enabled him to sort the elements in order of increasing atomic number.



You can think of the atomic number as a kind of serial number of an element, commencing at 1 for hydrogen and increasing by one for each successive element. The chemical name of the element and its symbol are uniquely tied to the atomic number; thus the symbol "Sr" stands for strontium, whose atoms all have Z = 38.

Mass number (A)

This is just the sum of the numbers of protons and neutrons in the nucleus. It is sometimes represented by the symbol A, so

$$A = Z + N \tag{2.4.1}$$

in which Z is the atomic number and N is the *neutron number*.

Nuclides and their Symbols

The term *nuclide* simply refers to any particular kind of nucleus. For example, a nucleus of atomic number 7 is a nuclide of nitrogen. Any nuclide is characterized by the pair of numbers (Z ,A). The element symbol depends on Z alone, so the symbol ^{26}Mg is used to specify the mass-26 nuclide of manganese, whose name implies Z=12. A more explicit way of denoting a particular kind of nucleus is to add the atomic number as a subscript. Of course, this is somewhat redundant, since the symbol Mg **always** implies Z=12, but it is sometimes a convenience when discussing several nuclides.

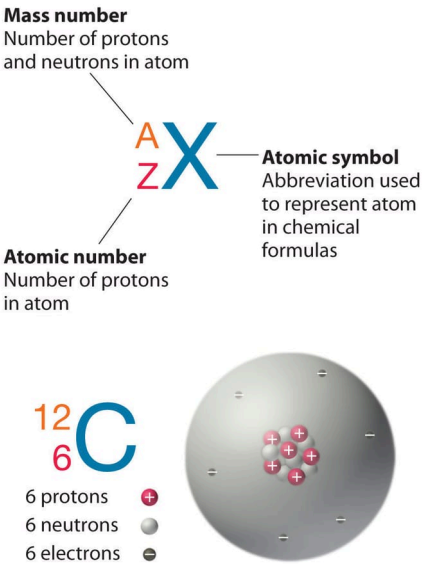


Figure 2.4.2: Formalism used for identifying specific nuclide (any particular kind of nucleus)

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.

Isotopes

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.

Two nuclides having the **same** atomic number but different mass numbers are known as *isotopes*. Most elements occur in nature as mixtures of isotopes, but twenty-three of them (including beryllium and fluorine, shown in the table) are monoisotopic. For example, there are three *natural isotopes* of magnesium: ^{24}Mg (79% of all Mg atoms), ^{25}Mg (10%), and ^{26}Mg (11%); all three are present in all compounds of magnesium in about these same proportions.

	Z	mass numbers
H	1	1 2 3
He	2	3 4
Li	3	6 7
Be	4	9
B	5	10 11
C	6	12 13 14
N	7	14 15
O	8	16 17 18
F	9	19
Ne	10	20 21 22

Approximately 290 isotopes occur in nature. The two heavy isotopes of hydrogen are especially important— so much so that they have names and symbols of their own:

$$\underset{\text{protium}}{{}^{1}_{1}\mathrm{H}} \tag{2.4.2}$$

$$\underset{\text{deuterium}}{{}^{2}_{1}\mathrm{H} \equiv \mathrm{D}} \tag{2.4.3}$$

$$\underset{\text{tritium}}{{}^{2}_{1}\mathrm{H} \equiv \mathrm{T}} \tag{2.4.4}$$

Deuterium accounts for only about 15 out of every one million atoms of hydrogen. Tritium, which is radioactive, is even less abundant. All the tritium on the earth is a by-product of the decay of other radioactive elements.

For carbon, 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 archeology. 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 2.4.2.

Table 2.4.2: 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
			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: https://youtu.be/ik6ZsaSyISo

Example 2.4.1

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 2.4.1

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

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

Summary

- The atom consists of discrete particles that govern its chemical and physical behavior.Contributors

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.

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2.5: 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:

$$C_3H_8\,(g) + 5\,O_2\,(g) \;\rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l) \tag{2.5.1}$$

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:

$$100 \text{ grams Water} \rightarrow 11.1 \text{ grams Hydrogen} + 88.9 \text{ grams Oxygen} \tag{2.5.2}$$

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:

$$\frac{\frac{88.9\ g\ Oxygen}{1\ atom}}{\frac{111\ g\ Hydrogen}{2\ atoms}} = 16 \tag{2.5.3}$$

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***

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 2.5.1). 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.

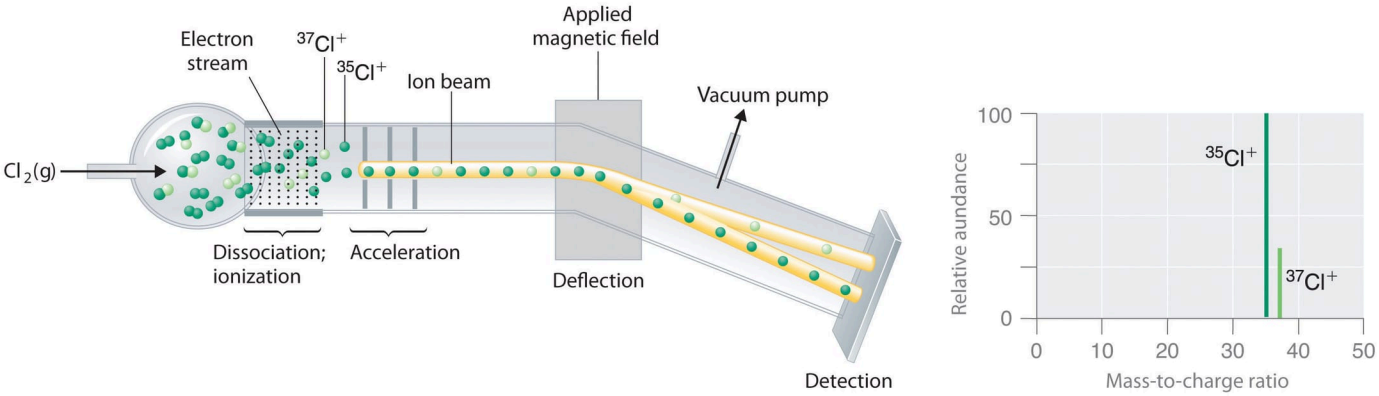


Figure 2.5.1: Determining Relative Atomic Masses Using a Mass Spectrometer. Chlorine consists of two isotopes, ^{35}Cl and ^{37}Cl, in approximately a 3:1 ratio. (a) When a sample of elemental chlorine is injected into the mass spectrometer, electrical energy is used to dissociate the Cl_2 molecules 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.

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

$$\frac{\text{mass of } ^{2}\text{H}}{\text{mass of } ^{12}\text{C}} \times \text{mass of } ^{12}\text{C} = 0.167842 \times 12 \text{ amu} = 2.104104 \text{ amu} \tag{2.5.4}$$

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:

$$(0.9889 \times 12 \text{ amu}) + (0.0111 \times 13.003355 \text{ amu}) = 12.01 \text{ amu} \tag{2.5.5}$$

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.

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Finding the Averaged Atomic Weight of an Element: https://youtu.be/bmP6Gr9zJiQ

Example 2.5.1: Bromine

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

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

$$^{79}\text{Br}: \frac{50.69}{100} = 0.5069 \tag{2.5.6}$$

$$^{81}\text{Br}: \frac{49.31}{100} = 0.4931 \tag{2.5.7}$$

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 2.5.1

Magnesium has the three isotopes listed in the following table:

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.

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 2.5.1

24.31 amu

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2.6: Introduction to 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 2.6.1). 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.

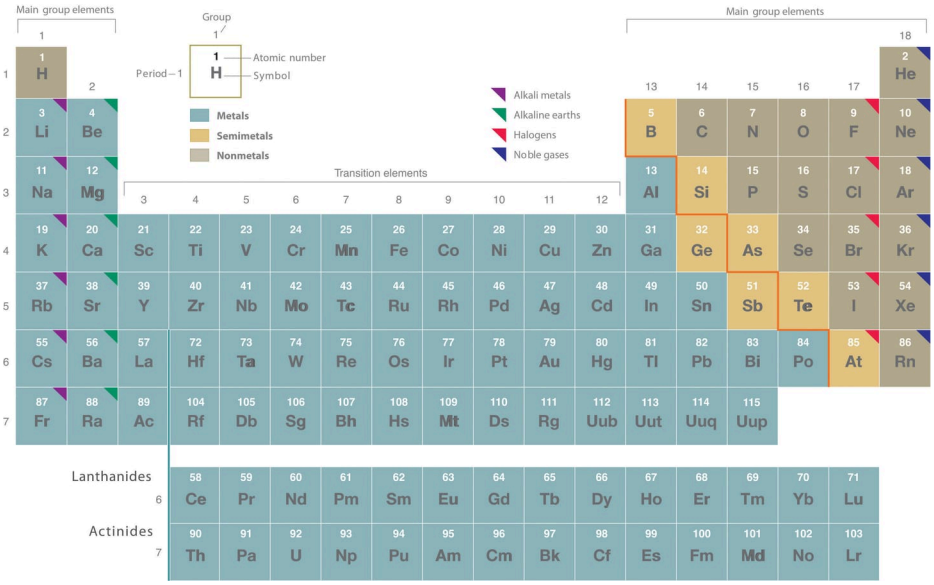


Figure 2.6.1: The Periodic Table Showing the Elements in Order of Increasing Z. The metals are on the bottom left in the periodic table, and the nonmetals are at the top right. The semimetals lie along a diagonal line separating the metals and nonmetals.

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 2.6.1 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 2.6.1

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 2.6.1 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 2.6.1, 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 2.6.1

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

Answer: metal

Descriptive Names

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.

Note

The noble gases are unreactive at room temperature and pressure.

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Periodic Law in the Periodic Table: https://youtu.be/ciJYvhRF5i4

Summary

- The periodic table is used as a predictive tool.

The periodic table is an arrangement 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.

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2.7: The Concept of Mole and the Avogadro Constant

$$2 \times \text{ atomic mass of carbon} = 2\,atoms\left(\frac{12.011\,amu}{atoms}\right) = 24.022\,amu \tag{2.7.1}$$

$$6 \times \text{ atomic mass of hydrogen} = 2\,atoms\left(\frac{1.0079\,amu}{atoms}\right) = 6.0474\,amu \tag{2.7.2}$$

$$1 \times \text{ atomic mass of oxygen} = 1\,atoms\left(\frac{15.9994\,amu}{atoms}\right) = 15.994\,amu \tag{2.7.3}$$

C Adding together the masses gives the molecular mass:

$$24.022\,amu + 6.0474\,amu + 15.9994\,amu = 46.069\,amu \tag{2.7.4}$$

Alternatively, we could have used unit conversions to reach the result in one step:

$$\left[2\,atomsC\left(\frac{12.011\,amu}{1\,atomC}\right)\right] + \left[6\,atomsH\left(\frac{1.0079\,amu}{1\,atomH}\right)\right] + \left[1\,atomsC\left(\frac{15.9994\,amu}{1\,atom0}\right)\right] = 46.069\,amu \tag{2.7.5}$$

The same calculation can also be done in a tabular format, which is especially helpful for more complex molecules:

$$2C \quad (2\,atoms)(12.011\,amu/atom) = 24.022\,amu \tag{2.7.6}$$

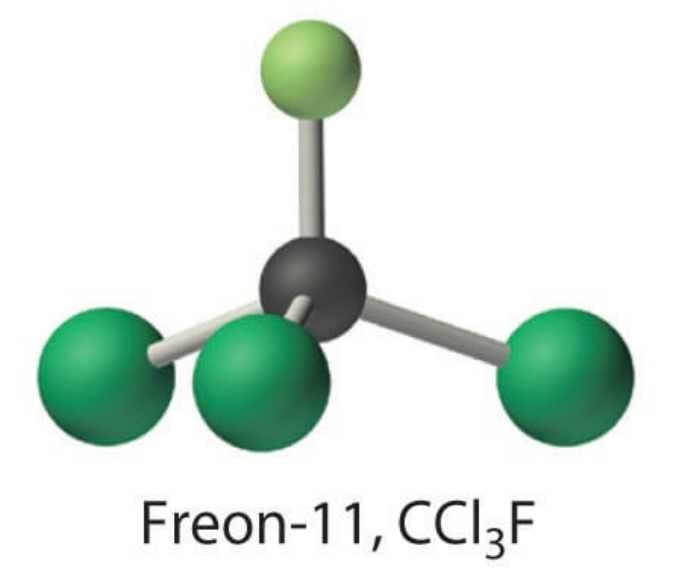
$$6H \quad (6\,atoms)(1.0079\,amu/atom) = 6.0474\,amu \tag{2.7.7}$$

$$+1O \quad (1\,atoms)(15.9994\,amu/atom) = 15.9994\,amu \tag{2.7.8}$$

$$C_2H_6O \quad \text{molecular mass of ethanol} = 46.069\,amu \tag{2.7.9}$$

Exercise 2.7.1: 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: 137.368 \,amu

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.

Note

Atomic mass, molecular mass, and formula mass all have the same units: atomic mass units.

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Determining the Molar Mass of a Molecule: https://youtu.be/wOjQjZqX7l8

Example 2.7.2: 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

$$3 \times \text{atomic mass of calcium} = 3\,atoms\left(\frac{40.078\,amu}{atom}\right) = 120.234\,amu \tag{2.7.10}$$

$$2 \times \text{atomic mass of phosphorus} = 2\,atoms\left(\frac{30.973761\,amu}{atom}\right) = 61.947522\,amu \tag{2.7.11}$$

$$8 \times \text{atomic mass of oxygen} = 8\,atoms\left(\frac{15.9994\,amu}{atom}\right) = 127.9952\,amu \tag{2.7.12}$$

C Adding together the masses gives the formula mass of $Ca_3(PO_4)_2$:

$$120.234\,amu + 61.947522\,amu + 127.9952\,amu = 310.177\,amu \tag{2.7.13}$$

We could also find the formula mass of Ca3(PO4)2 in one step by using unit conversions or a tabular format:

$$\left[3\,atoms Ca\left(\frac{40.078\,amu}{1\,atom Ca}\right)\right] + \left[2\,atoms P\left(\frac{30.973761\,amu}{1\,atom P}\right)\right] + \left[8\,atoms O\left(\frac{15.9994\,amu}{1\,atom O}\right)\right] \tag{2.7.14}$$

$$= 310.177\,amu \tag{2.7.15}$$

$$3Ca \quad (3\,atoms)(40.078\,amu/atom) = 120.234\,amu \tag{2.7.16}$$

$$2P \quad (2\,atoms)(30.973761\,amu/atom) = 61.947522\,amu \tag{2.7.17}$$

$$+8O \quad (8\,atoms)(15.9994\,amu/atom) = 127.9952\,amu \tag{2.7.18}$$

$$Ca_3P_2O_8 \quad \text{formula mass of } Ca_3(PO_4)_2 = 310.177\,amu \tag{2.7.19}$$

$$(moles)(molarmass) \rightarrow mass \tag{2.7.20}$$

or, more specifically,

$$moles\left(\frac{grams}{mole}\right) = grams \tag{2.7.21}$$

Conversely, to convert the mass of a substance to moles:

$$\left(\frac{grams}{molarmass}\right) \rightarrow moles \tag{2.7.22}$$

$$\left(\frac{grams}{grams/mole}\right) = grams\left(\frac{mole}{grams}\right) = moles \tag{2.7.23}$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \tag{2.7.24}$$

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?

$$(1.57\ mol\ O_2)\left(\frac{2\ mol H_2O}{1\ mol\ O_2}\right) = 3.14\ mol\ H_2O \tag{2.7.25}$$

The ratio $\left(\frac{2\ mol\ H_2O}{1\ mol\ O_2}\right)$ is the stoichiometric relationship between H_2O and O_2 from the balanced equation for this reaction.

Example 2.7.3

For the combustion of butane (C_4H_{10}) the balanced equation is:

$$2C_4H_{10(l)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)} \tag{2.7.26}$$

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:

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ C_4H_{10} \tag{2.7.27}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \tag{2.7.28}$$

Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ C_4H_{10} = 6.88 \times 10^{-2}\ mol\ CO_2 \tag{2.7.29}$$

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):

$$6.88 \times 10^{-2}\ mol\ CO_2\left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2}\right) = 3.03\ g\ CO_2 \tag{2.7.30}$$

Be sure to pay attention to the units when converting between mass and moles. Figure 2.7.1 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 Example 2.7.3 and Example 2.7.4.

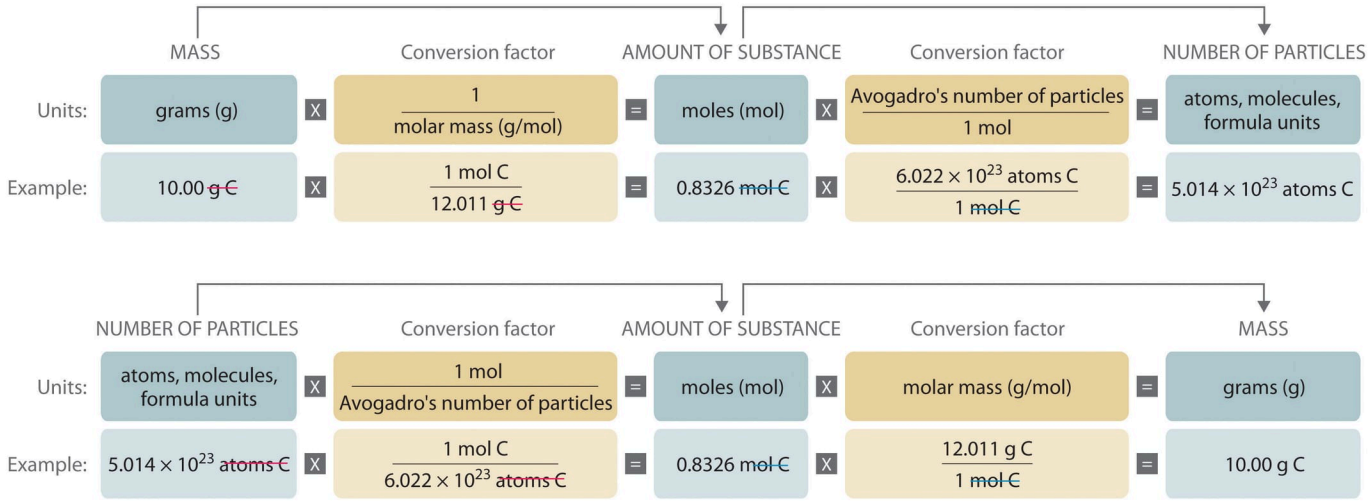


Figure 2.7.1: A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units

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

Conversions Between Grams, Mol, & Atoms: https://youtu.be/rOvErpAnoCg

Example 2.7.4

For 35.00 g of ethylene glycol ($HOCH_2CH_2OH$), 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. **A** The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 2.7.2.7.1:

$$2C(2\,atoms)(12.011\,amu/atom) = 24.022\,amu \tag{2.7.31}$$

$$6H(6\,atoms)(1.0079\,amu/atom) = 6.0474\,amu \tag{2.7.32}$$

$$2O(2\,atoms)(15.9994\,amu/atom) = 31.9988\,amu \tag{2.7.33}$$

$$C_2H_6O_2\text{molecular mass of ethylene glycol} = 62.068\,amu \tag{2.7.34}$$

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):

$$\frac{\text{mass of ethylene glycol (g)}}{\text{molar mass (g/mol)}} = \text{moles ethylene glycol (mol)} \tag{2.7.35}$$

So

$$35.00\,g\text{ethylene glycol}\left(\frac{1\,mole\text{ethylene glycol}}{62.068\,g\text{ethylene glycol}}\right) = 0.5639\,mol\text{ethylene glycol} \tag{2.7.36}$$

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.

b. **C** To calculate the number of molecules in the sample, we multiply the number of moles by Avogadro's number:

$$\text{molecules of ethylene glycol} = 0.5639\,mol\left(\frac{6.022\times10^{23}\,molecules}{1\,mol}\right) \tag{2.7.37}$$

$$= 3.396\times10^{23}\,molecules \tag{2.7.38}$$

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.

$$2S(2\,atoms)(32.065\,amu/atom) = 64.130\,amu \tag{2.7.39}$$

$$+2Cl(2\,atoms)(35.453\,amu/atom) = 70.906\,amu \tag{2.7.40}$$

$$S_2Cl_2\text{molecular mass of } S_2Cl_2 = 135.036\,amu \tag{2.7.41}$$

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:

$$moles S_2Cl_2\left[\text{molar mass}\left(\frac{g}{mol}\right)\right] \rightarrow mass of S_2Cl_2\,(g) \tag{2.7.42}$$

$$1.75\,mol S_2Cl_2\left(\frac{135.036\,g S_2Cl_2}{1\,mol S_2Cl_2}\right) = 236\,g S_2Cl_2 \tag{2.7.43}$$

b.

A The formula mass of $Ca(ClO)_2$ is obtained as follows:

$$1Ca(1\,atom)(40.078\,amu/atom) = 40.078\,amu \tag{2.7.44}$$

$$2Cl(2\,atoms)(35.453\,amu/atom) = 70.906\,amu \tag{2.7.45}$$

$$+2O(2\,atoms)(15.9994\,amu/atom) = 31.9988\,amu \tag{2.7.46}$$

$$Ca(ClO)_2\text{ formula mass of } Ca(ClO)_2 = 142.983\,amu \tag{2.7.47}$$

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:

$$moles Ca(ClO)_2\left[\frac{\text{molar mass} Ca(ClO)_2}{1\,mol Ca(ClO)_2}\right] = mass Ca(ClO)_2 \tag{2.7.48}$$

$$1.75\,mol Ca(ClO)_2\left[\frac{142.983\,g Ca(ClO)_2}{1\,mol Ca(ClO)_2}\right] = 250\,g Ca(ClO)_2 \tag{2.7.49}$$

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 2.7.5

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. 1.71 g
b. 0.721 g

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:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \tag{2.7.50}$$

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?

$$(1.57\ mol\ O_2)\left(\frac{2\ mol H_2O}{1\ mol\ O_2}\right) = 3.14\ mol\ H_2O \tag{2.7.51}$$

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 2.7.6

For the combustion of butane (C_4H_{10}) the balanced equation is:

$$2C_4H_{10(l)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)} \tag{2.7.52}$$

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:

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ C_4H_{10} \tag{2.7.53}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \tag{2.7.54}$$

Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ C_4H_{10} = 6.88 \times 10^{-2}\ mol\ CO_2 \tag{2.7.55}$$

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):

$$6.88 \times 10^{-2}\ mol\ CO_2\left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2}\right) = 3.03\ g\ CO_2 \tag{2.7.56}$$

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.

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.

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2.8: Using the Mole Concept in Calculations

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3: CHEMICAL COMPOUNDS

3.1: Types of Chemical Compounds and their Formulas

3.2: The Mole Concept and Chemical Compounds

3.3: Composition of Chemical Compounds

3.4: Oxidation States: A Useful Tool in Describing Chemical Compounds

3.5: Importance of Nomenclature

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3.7: Names of Formulas of Organic Compounds

3.E: Homework Problems

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3.1: Types of Chemical Compounds and their Formulas

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.

Note

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 $3.1.1$). 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 $3.1.1$).

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.

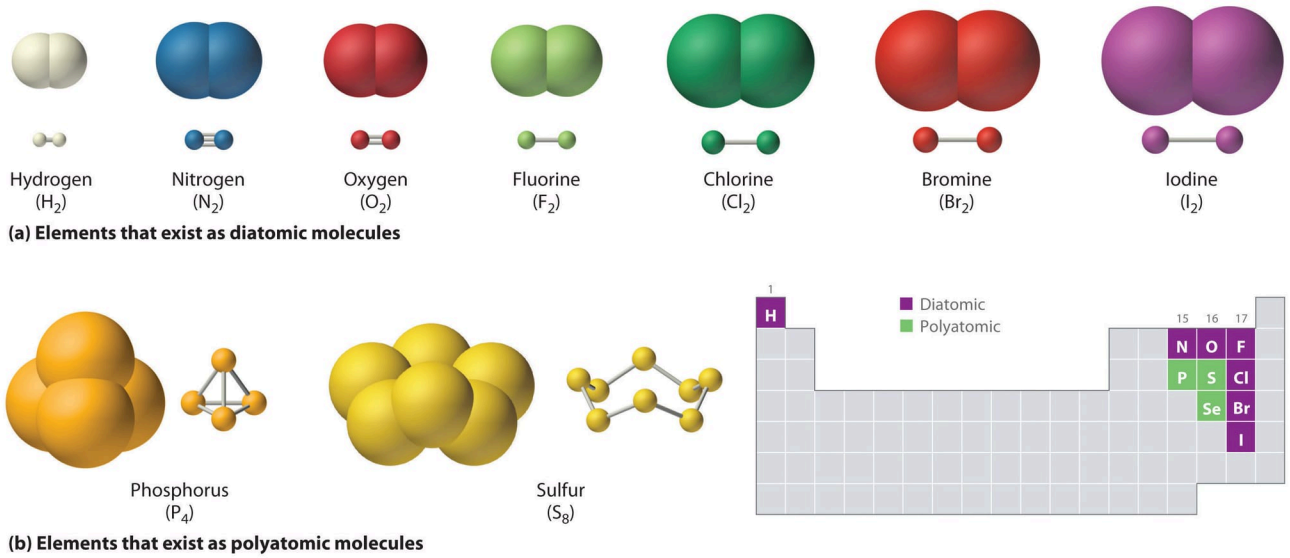


Figure 3.1.1: Elements That Exist as Covalent Molecules. (a) Several elements naturally exist as diatomic molecules, in which two atoms (E) are joined by one or more covalent bonds to form a molecule with the general formula E2. (b) A few elements naturally exist as polyatomic molecules, which contain 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.

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 elswhere.

Note

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 3.1.1

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 $\mathrm{C_2H_6O}$.

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 3.1.1

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. N_2O
b. $C_{12}H_{22}O_{11}$
c. SF_6

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.

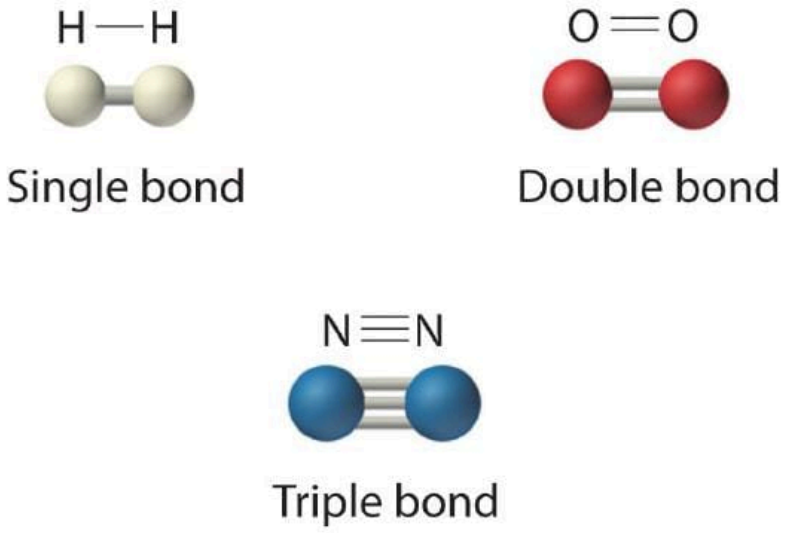


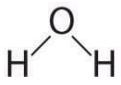
Figure 3.1.2: Molecules That Contain Single, Double, and Triple Bonds. Hydrogen (H_2) has a single bond between atoms. Oxygen (O_2) has a double bond between atoms, indicated by two lines (=). Nitrogen (N_2) has a triple bond between atoms, indicated by three lines (≡). Each bond represents an electron 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 (Figure 3.1.2). 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 3.1.1).

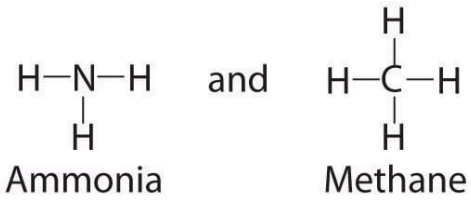
Table 3.1.1: The Number of Bonds That Selected Atoms Commonly Form to Other Atoms

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:



As shown in Figure 3.1.3, however, the actual three-dimensional structure of NH_3 looks like a pyramid with a triangular base of three hydrogen atoms. The structure of CH_4, with four hydrogen atoms arranged around a central carbon atom as shown in Figure 3.1.3, 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.

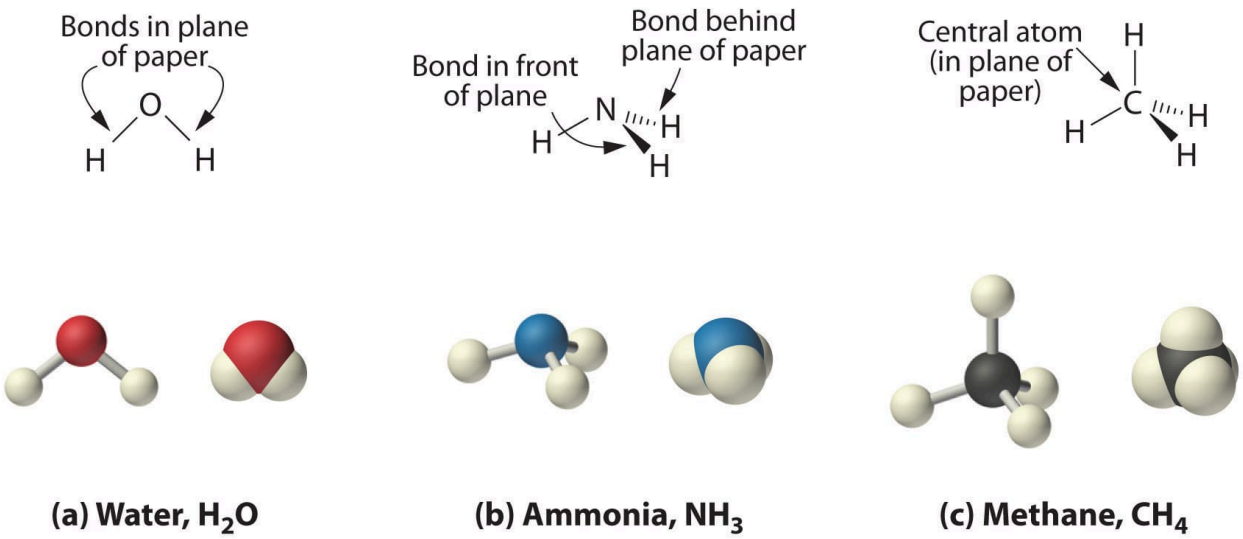


Figure 3.1.3: The Three-Dimensional Structures of Water, Ammonia, and Methane. (a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.

Figures 3.1.3-3.1.3 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 3.1.4 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 (part (a) in Figure 3.1.4) gives only the number of each kind of atom; writing methanol as CH_4O tells nothing about its structure. In contrast, the structural formula (part (b) in Figure 3.1.4) 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 3.1.4) and the perspective drawing (part (d) in Figure 3.1.4) 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 3.1.4) 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."

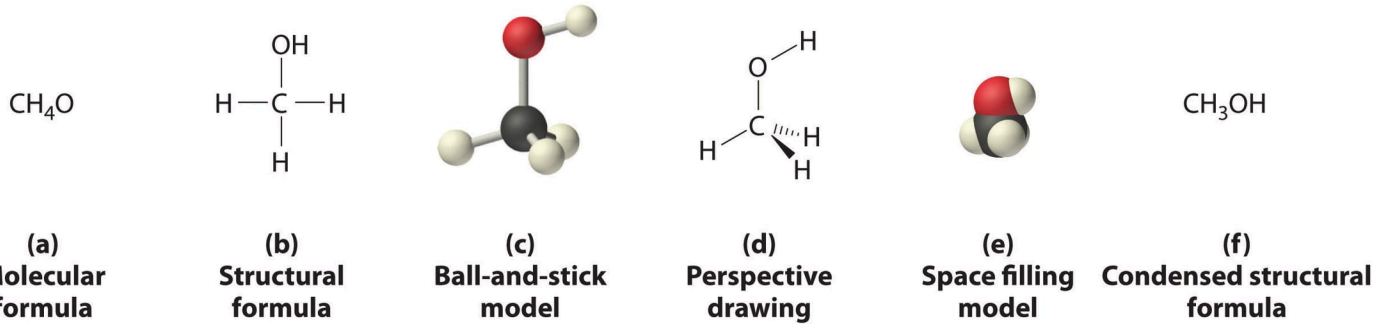


Figure 3.1.4: Different Ways of Representing the Structure of a Molecule. (a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (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 3.1.4), 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 3.1.2

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.

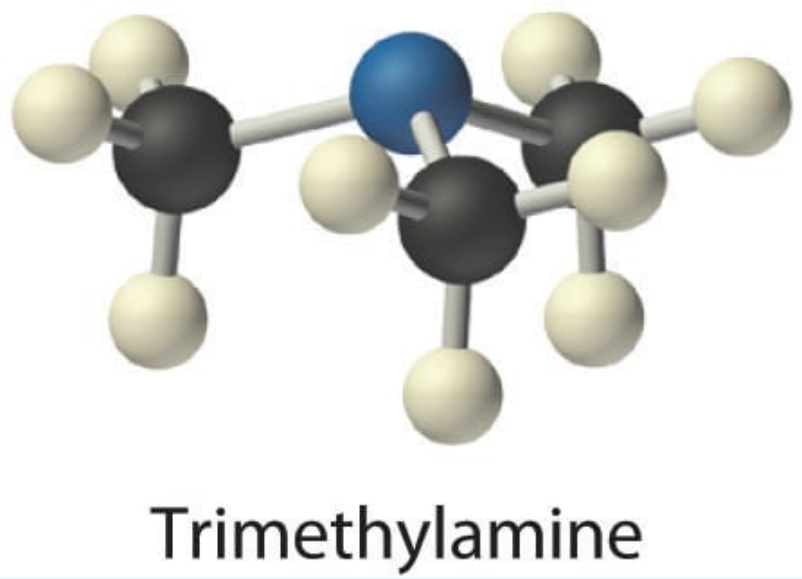
Solution:

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.



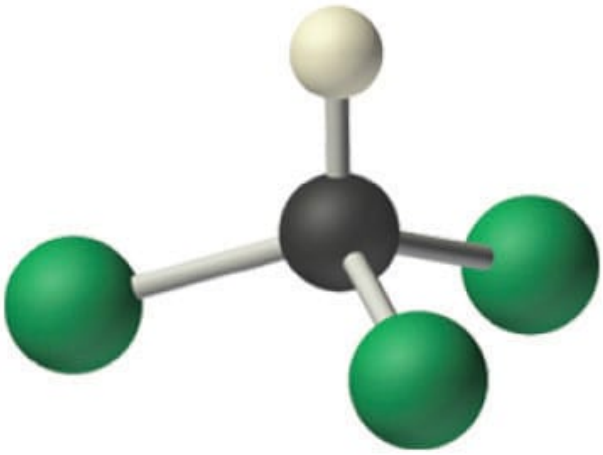
Exercise 3.1.2

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 $CHCl_3$.

b. Hydrazine is used as a propellant in the attitude jets of the space shuttle. Its condensed structural formula is H_2NNH_2.

c. Putrescine is a pungent-smelling compound first isolated from extracts of rotting meat. Its condensed structural formula is $H_2NCH_2CH_2CH_2CH_2NH_2$. This is often written as $H_2N(CH_2)_4NH_2$ to indicate that there are four CH_2 fragments linked together.



Answer a available at the end of this section.

Ionic Compounds

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.

Note

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

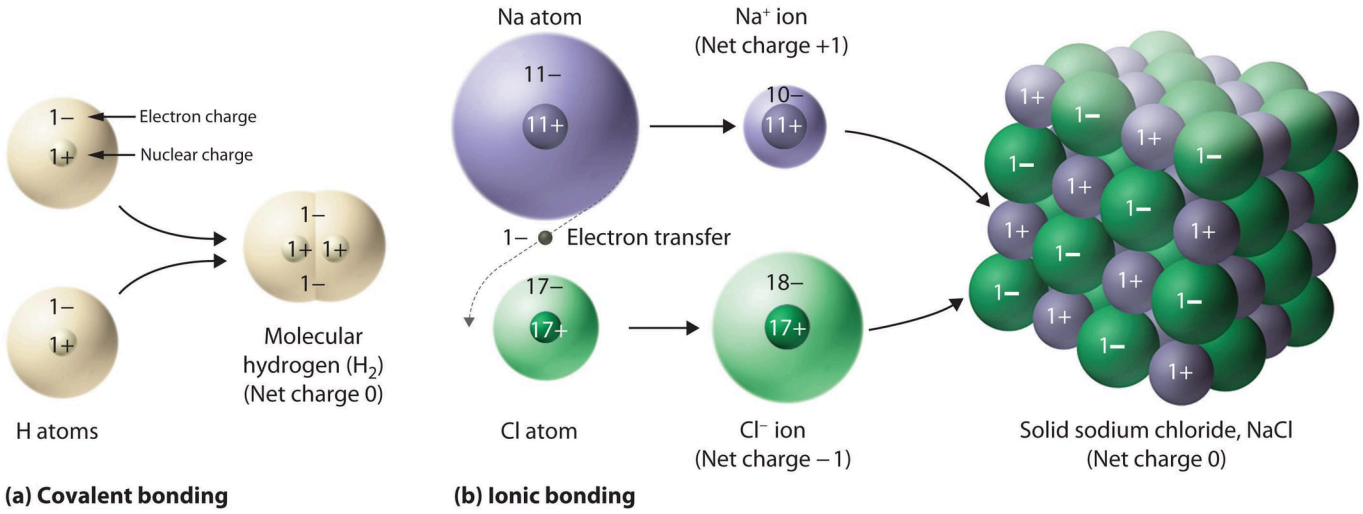


Figure 3.1.5: Covalent and Ionic Bonding. (a) In molecular hydrogen (H_2), two hydrogen atoms share two electrons to form a covalent bond. (b) The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting Na^+ and Cl^- ions form a three-dimensional solid that is held together by attractive electrostatic interactions.

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 3.1.5). As shown in Equation 3.1.1, 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:

$$\text{electrostatic energy} \propto \frac{Q_1 Q_2}{r} \tag{3.1.1}$$

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. As shown in Figure 3.1.6, 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.

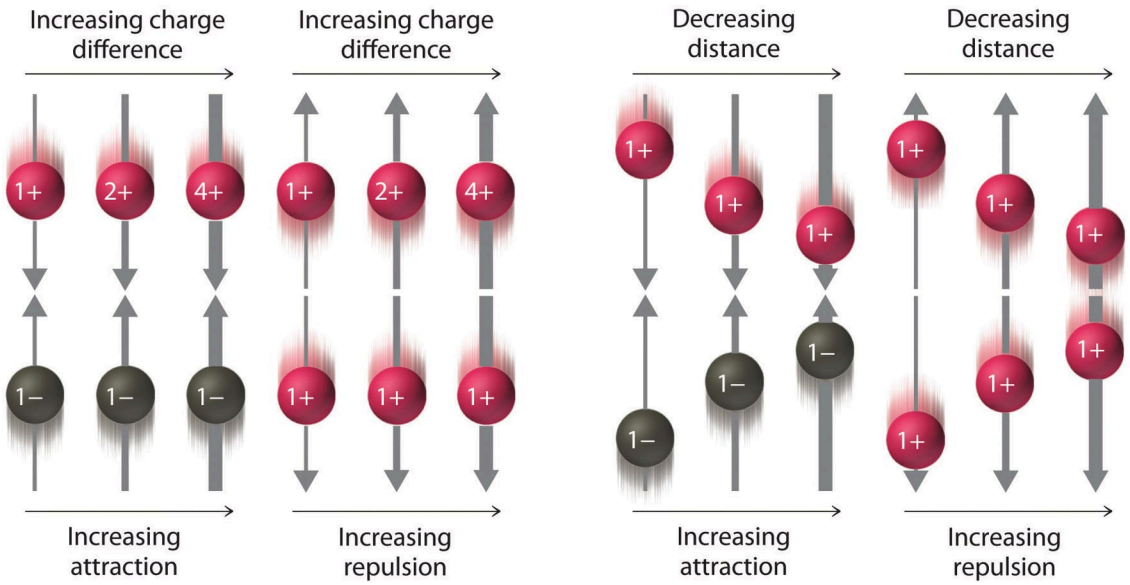


Figure 3.1.6: The Effect of Charge and Distance on the Strength of Electrostatic Interactions. As the charge on ions increases or the distance between ions decreases, so does the strength of the attractive (−...+) or repulsive (−...− or +...+) interactions. The strength of these interactions is represented by the thickness of the arrows.

Note

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), 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 3.1.5. 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.

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, as discussed in Section 2.3. Some common monatomic ions are listed in Table 3.1.2.

Note

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 3.1.2: 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 3.1.3

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 3.1.3

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. Ca^{2+}
b. I^{-}
c. Zr^{4+}

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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 part (a) in Figure 3.1.8 which shows the three-dimensional array of alternating positive and negative ions held together by strong electrostatic attractions. In contrast, as shown in part (b) in Figure 3.1.8 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). 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 CH_4 molecules. A comparison of the different physical properties of ionic compounds and covalent molecular substances is given in Table 3.1.3.

Table 3.1.3: 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

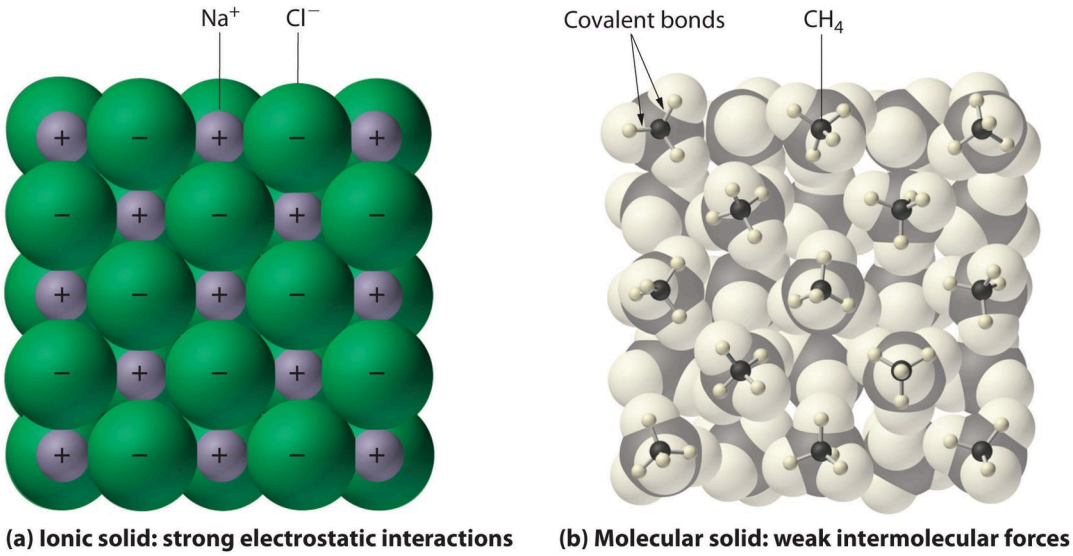


Figure 3.1.8: Interactions in Ionic and Covalent Solids. (a) The positively and negatively charged ions in an ionic solid such as sodium chloride (NaCl) are held together by strong electrostatic interactions. (b) In this representation of the packing of methane (CH4) molecules in solid methane, a prototypical 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.

- **The Learning Objective of this Module is to describe the composition of a chemical compound.**

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 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 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 C_2H_5, but it contains two C_2H_5 formula units, giving a molecular formula of C_4H_{10}.

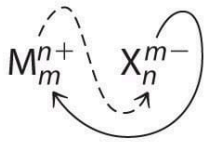
Because ionic compounds do not contain discrete molecules, empirical formulas are used to indicate their compositions. All compounds, whether ionic or covalent, must be electrically neutral. Consequently, the positive and negative charges in a formula unit must exactly cancel each other. If the cation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

Note

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

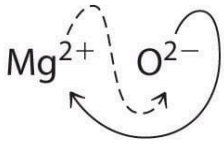
Binary Ionic Compounds

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 $MgCl_2$, 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 Mg^{2+} and O^{2-}. Using the absolute values of the charges on the ions as subscripts gives the formula 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 3.1.4

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:

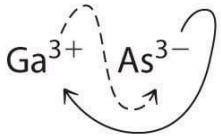
A If not given, determine the ionic charges based on the location of the elements in the periodic table.

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.

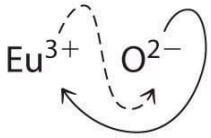
Solution

a. **B** Using the absolute values of the charges on the ions as the subscripts gives Ga3As3:



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.

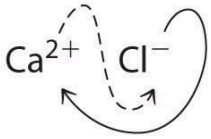
b. **B** Because Eu^{3+} has a charge of +3 and O^{2-} has a charge of −2, a 1:1 compound would have a net charge of +1. We must therefore find multiples of the charges that cancel. We cross charges, using the absolute value of the charge on one ion as the subscript for the other ion:



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 3.1.4

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. Li_3N
b. Al_2O_3
c. Li_2O

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 3.1.4.

Table 3.1.4: Common Polyatomic Ions and Their Names

Formula	Name of Ion
NH_4^+	ammonium
$CH_3NH_3^+$	methylammonium
OH^-	hydroxide
O_2^{2-}	peroxide
CN^-	cyanide
SCN^-	thiocyanate
NO_2^-	nitrite
NO_3^-	nitrate
CO_3^{2-}	carbonate
HCO_3^-	hydrogen carbonate, or bicarbonate
SO_3^{2-}	sulfite

Formula	Name of Ion
SO_4^{2-}	sulfate
HSO_4^-	hydrogen sulfate, or bisulfate
PO_4^{3-}	phosphate
HPO_4^{2-}	hydrogen phosphate
$H_2PO_4^-$	dihydrogen phosphate
ClO^-	hypochlorite
ClO_2^-	chlorite
ClO_3^-	chlorate
ClO_4^-	perchlorate
MnO_4^-	permanganate
$CrO4_2^-$	chromate
$Cr_2O_7^{2-}$	dichromate
$C_2O_4^{2-}$	oxalate
HCO_2^-	formate
$CH_3CO_2^-$	acetate
$C_6H_5CO_2^-$	benzoate

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 3.1.5

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 3.1.4 "Common Polyatomic Ions and Their Names" 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 3.1.5

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

Answer:

a. $Ca(H_2PO_4)_2$: calcium dihydrogen phosphate is one of the ingredients in baking powder.
b. $NaHCO_3$: sodium bicarbonate is found in antacids and baking powder; in pure form, it is sold as baking soda.
c. $(NH_4)_2SO_4$: ammonium sulfate is a common source of nitrogen in fertilizers.

Summary

- There are two fundamentally different kinds of chemical bonds (covalent and ionic) that cause substances to have very different properties.
- The composition of a compound is represented by an empirical or molecular formula, each consisting of at least one formula unit.Contributors

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. Most covalent compounds consist of molecules, groups of atoms in which one or more pairs of electrons are shared by at least two atoms to form a covalent bond. The atoms in molecules are held together by the electrostatic attraction between the positively charged nuclei of the bonded atoms and the negatively charged electrons shared by the nuclei. 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. Single bonds, double bonds, and triple bonds are covalent bonds in which one, two, and three pairs of electrons, respectively, are shared between two bonded atoms. 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. 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.

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 3.1.2

$CHCl_3$

N_2H_4

$C_4H_{12}N_2$

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3.2: The Mole Concept and Chemical Compounds

$$2 \times \text{ atomic mass of carbon} = 2\,atoms\left(\frac{12.011\,amu}{atoms}\right) = 24.022\,amu \tag{3.2.1}$$

$$6 \times \text{ atomic mass of hydrogen} = 2\,atoms\left(\frac{1.0079\,amu}{atoms}\right) = 6.0474\,amu \tag{3.2.2}$$

$$1 \times \text{ atomic mass of oxygen} = 1\,atoms\left(\frac{15.9994\,amu}{atoms}\right) = 15.994\,amu \tag{3.2.3}$$

C Adding together the masses gives the molecular mass:

$$24.022\,amu + 6.0474\,amu + 15.9994\,amu = 46.069\,amu \tag{3.2.4}$$

Alternatively, we could have used unit conversions to reach the result in one step:

$$\left[2\,atomsC\left(\frac{12.011\,amu}{1\,atomC}\right)\right] + \left[6\,atomsH\left(\frac{1.0079\,amu}{1\,atomH}\right)\right] + \left[1\,atomsC\left(\frac{15.9994\,amu}{1\,atom0}\right)\right] = 46.069\,amu \tag{3.2.5}$$

The same calculation can also be done in a tabular format, which is especially helpful for more complex molecules:

$$2C \quad (2\,atoms)(12.011\,amu/atom) = 24.022\,amu \tag{3.2.6}$$

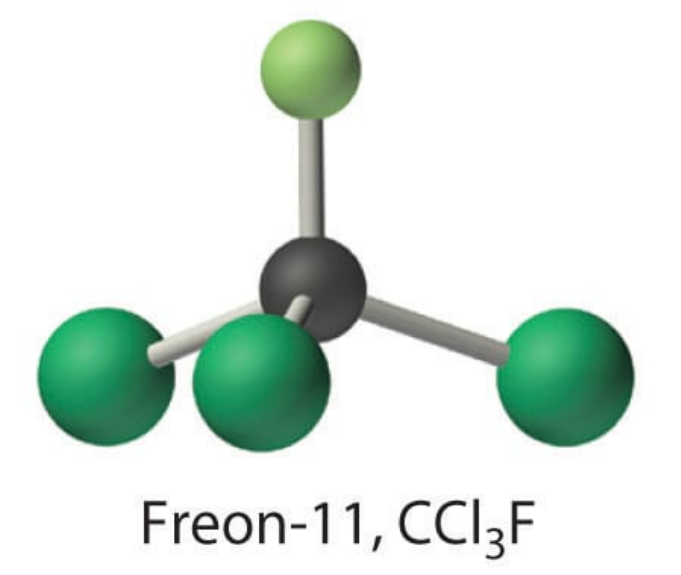
$$6H \quad (6\,atoms)(1.0079\,amu/atom) = 6.0474\,amu \tag{3.2.7}$$

$$+1O \quad (1\,atoms)(15.9994\,amu/atom) = 15.9994\,amu \tag{3.2.8}$$

$$C_2H_6O \quad \text{molecular mass of ethanol} = 46.069\,amu \tag{3.2.9}$$

Exercise 3.2.1: 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: 137.368 \,amu

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.

Note

Atomic mass, molecular mass, and formula mass all have the same units: atomic mass units.

Example 3.2.2: 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

$$3 \times \text{atomic mass of calcium} = 3\,atoms\left(\frac{40.078\,amu}{atom}\right) = 120.234\,amu \tag{3.2.10}$$

$$2 \times \text{atomic mass of phosphorus} = 2\,atoms\left(\frac{30.973761\,amu}{atom}\right) = 61.947522\,amu \tag{3.2.11}$$

$$8 \times \text{atomic mass of oxygen} = 8\,atoms\left(\frac{15.9994\,amu}{atom}\right) = 127.9952\,amu \tag{3.2.12}$$

C Adding together the masses gives the formula mass of $Ca_3(PO_4)_2$:

$$120.234\,amu + 61.947522\,amu + 127.9952\,amu = 310.177\,amu \tag{3.2.13}$$

We could also find the formula mass of Ca3(PO4)2 in one step by using unit conversions or a tabular format:

$$\left[3\,atoms Ca\left(\frac{40.078\,amu}{1\,atom Ca}\right)\right] + \left[2\,atoms P\left(\frac{30.973761\,amu}{1\,atom P}\right)\right] + \left[8\,atoms O\left(\frac{15.9994\,amu}{1\,atom O}\right)\right] \tag{3.2.14}$$

$$= 310.177\,amu \tag{3.2.15}$$

$$3Ca \quad (3\,atoms)(40.078\,amu/atom) = 120.234\,amu \tag{3.2.16}$$

$$2P \quad (2\,atoms)(30.973761\,amu/atom) = 61.947522\,amu \tag{3.2.17}$$

$$+8O \quad (8\,atoms)(15.9994\,amu/atom) = 127.9952\,amu \tag{3.2.18}$$

$$Ca_3P_2O_8 \quad \text{formula mass of } Ca_3(PO_4)_2 = 310.177\,amu \tag{3.2.19}$$

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Molar Masses of Compounds: https://youtu.be/PhOqgNNv78s

$$(moles)(molarmass) \rightarrow mass \tag{3.2.20}$$

or, more specifically,

$$moles\left(\frac{grams}{mole}\right) = grams \tag{3.2.21}$$

Conversely, to convert the mass of a substance to moles:

$$\left(\frac{grams}{molarmass}\right) \rightarrow moles \tag{3.2.22}$$

$$\left(\frac{grams}{grams/mole}\right) = grams\left(\frac{mole}{grams}\right) = moles \tag{3.2.23}$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \tag{3.2.24}$$

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?

$$(1.57\ mol\ O_2)\left(\frac{2\ mol H_2O}{1\ mol\ O_2}\right) = 3.14\ mol\ H_2O \tag{3.2.25}$$

The ratio $\left(\frac{2\ mol\ H_2O}{1\ mol\ O_2}\right)$ is the stoichiometric relationship between H_2O and O_2 from the balanced equation for this reaction.

Example 3.2.3

For the combustion of butane (C_4H_{10}) the balanced equation is:

$$2C_4H_{10(l)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)} \tag{3.2.26}$$

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:

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ C_4H_{10} \tag{3.2.27}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \tag{3.2.28}$$

Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ C_4H_{10} = 6.88 \times 10^{-2}\ mol\ CO_2 \tag{3.2.29}$$

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):

$$6.88 \times 10^{-2}\ mol\ CO_2\left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2}\right) = 3.03\ g\ CO_2 \tag{3.2.30}$$

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Conversions Between Grams, Mol, & Atoms: https://youtu.be/rOvErpAnoCg

Be sure to pay attention to the units when converting between mass and moles. Figure 3.2.1 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 Example 3.2.3 and Example 3.2.4.

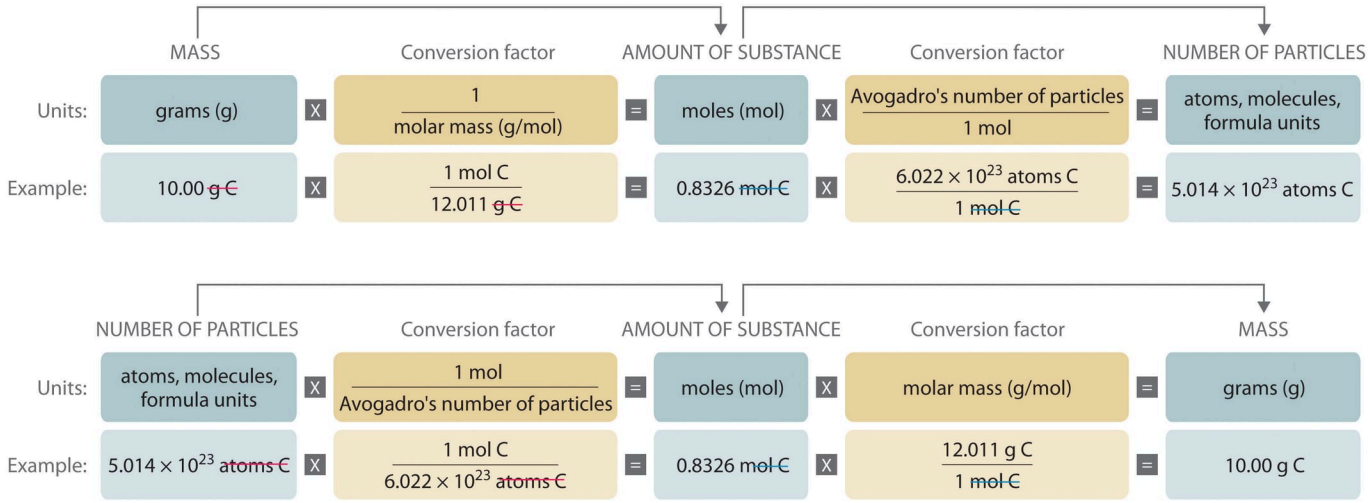


Figure 3.2.1: A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units

Example 3.2.4

For 35.00 g of ethylene glycol ($HOCH_2CH_2OH$), 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. **A** The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 3.2.3.2.1:

$$2C(2\,atoms)(12.011\,amu/atom) = 24.022\,amu \tag{3.2.31}$$

$$6H(6\,atoms)(1.0079\,amu/atom) = 6.0474\,amu \tag{3.2.32}$$

$$2O(2\,atoms)(15.9994\,amu/atom) = 31.9988\,amu \tag{3.2.33}$$

$$C_2H_6O_2\text{molecular mass of ethylene glycol} = 62.068\,amu \tag{3.2.34}$$

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):

$$\frac{\text{mass of ethylene glycol (g)}}{\text{molar mass (g/mol)}} = \text{moles ethylene glycol (mol)} \tag{3.2.35}$$

So

$$35.00\,g\text{ethylene glycol}\left(\frac{1\,mole\text{ethylene glycol}}{62.068\,g\text{ethylene glycol}}\right)=0.5639\,mol\text{ethylene glycol} \tag{3.2.36}$$

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.

b. **C** To calculate the number of molecules in the sample, we multiply the number of moles by Avogadro's number:

$$\text{molecules of ethylene glycol}=0.5639\,mol\left(\frac{6.022\times10^{23}\,molecules}{1\,mol}\right) \tag{3.2.37}$$

$$=3.396\times10^{23}\,molecules \tag{3.2.38}$$

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.

$$2S(2\,atoms)(32.065\,amu/atom)=64.130\,amu \tag{3.2.39}$$

$$+2Cl(2\,atoms)(35.453\,amu/atom)=70.906\,amu \tag{3.2.40}$$

$$S_2Cl_2\text{molecular mass of }S_2Cl_2=135.036\,amu \tag{3.2.41}$$

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:

$$molesS_2Cl_2\left[\text{molar mass}\left(\frac{g}{mol}\right)\right]\rightarrow massofS_2Cl_2\,(g) \tag{3.2.42}$$

$$1.75\,molS_2Cl_2\left(\frac{135.036\,gS_2Cl_2}{1\,molS_2Cl_2}\right)=236\,gS_2Cl_2 \tag{3.2.43}$$

b.

A The formula mass of $Ca(ClO)_2$ is obtained as follows:

$$1Ca(1\,atom)(40.078\,amu/atom)=40.078\,amu \tag{3.2.44}$$

$$2Cl(2\,atoms)(35.453\,amu/atom)=70.906\,amu \tag{3.2.45}$$

$$+2O(2\,atoms)(15.9994\,amu/atom)=31.9988\,amu \tag{3.2.46}$$

$$Ca(ClO)_2\text{ formula mass of }Ca(ClO)_2=142.983\,amu \tag{3.2.47}$$

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:

$$molesCa(ClO)_2\left[\frac{\text{molar mass}Ca(ClO)_2}{1\,molCa(ClO)_2}\right]=massCa(ClO)_2 \tag{3.2.48}$$

$$1.75\,molCa(ClO)_2\left[\frac{142.983\,gCa(ClO)_2}{1\,molCa(ClO)_2}\right]=250\,gCa(ClO)_2 \tag{3.2.49}$$

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 3.2.5

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. 1.71 g
b. 0.721 g

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:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \tag{3.2.50}$$

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?

$$(1.57\ mol\ O_2)\left(\frac{2\ mol H_2O}{1\ mol\ O_2}\right) = 3.14\ mol\ H_2O \tag{3.2.51}$$

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 3.2.6

For the combustion of butane (C_4H_{10}) the balanced equation is:

$$2C_4H_{10(l)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)} \tag{3.2.52}$$

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:

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ C_4H_{10} \tag{3.2.53}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \tag{3.2.54}$$

Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ C_4H_{10} = 6.88 \times 10^{-2}\ mol\ CO_2 \tag{3.2.55}$$

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):

$$6.88 \times 10^{-2}\ mol\ CO_2 \left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2}\right) = 3.03\ g\ CO_2 \tag{3.2.56}$$

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): https://youtu.be/74mHV0CZcjw

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.

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3.3: Composition of Chemical Compounds

$$2 \times (1.0079\ amu) + 1 \times (15.9994\ amu) = 18.01528\ amu \tag{3.3.1}$$

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:

$$6 \times (12\ amu) + 12 \times (1.00794\ amu) + 6 \times (15.9994\ amu) = 180.0\ amu \tag{3.3.2}$$

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:

$$23.0\ amu + 35.5\ amu = 58.5\ amu \tag{3.3.3}$$

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:

$$1 \times (12.011\ amu) + 4 \times (1.008) = 16.043\ amu \tag{3.3.4}$$

the relative (mass) percentages of carbon and hydrogen are

$$\%C = \frac{1 \times (12.011\ amu)}{16.043 amu} = 0.749 = 74.9\% \tag{3.3.5}$$

$$\%H = \frac{4 \times (1.008\ amu)}{16.043\ amu} = 0.251 = 25.1\% \tag{3.3.6}$$

A more complex example is sucrose (table sugar) 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:

$$\text{mass of C/mol of sucrose} = 12\,mol\,C \times \frac{12.011\,g\,C}{1\,mol\,C} = 144.132\,g\,C \tag{3.3.7}$$

$$\text{mass of H/mol of sucrose} = 22\,mol\,H \times \frac{1.008\,g\,H}{1\,mol\,H} = 22.176\,g\,C \tag{3.3.8}$$

$$\text{mass of O/mol of sucrose} = 11\,mol\,O \times \frac{15.999\,g\,O}{1\,mol\,O} = 175.989\,g\,O \tag{3.3.9}$$

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:

$$\text{mass} = \frac{\text{mass of C/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{144.132\,g\,C}{342.297\,g/mol} \times 100 = 42.12\% \tag{3.3.10}$$

$$\text{mass} = \frac{\text{mass of H/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{22.176\,g\,H}{342.297\,g/mol} \times 100 = 6.48\% \tag{3.3.11}$$

$$\text{mass} = \frac{\text{mass of O/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{175.989\,g\,O}{342.297\,g/mol} \times 100 = 51.41\% \tag{3.3.12}$$

This can be checked by verifying that the sum of the percentages of all the elements in the compound is 100%:

$$42.12\% + 6.48\% + 51.41\% = 100.01\% \tag{3.3.13}$$

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 42.12 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 42.12% carbon, 6.48% hydrogen, and 51.41% oxygen.

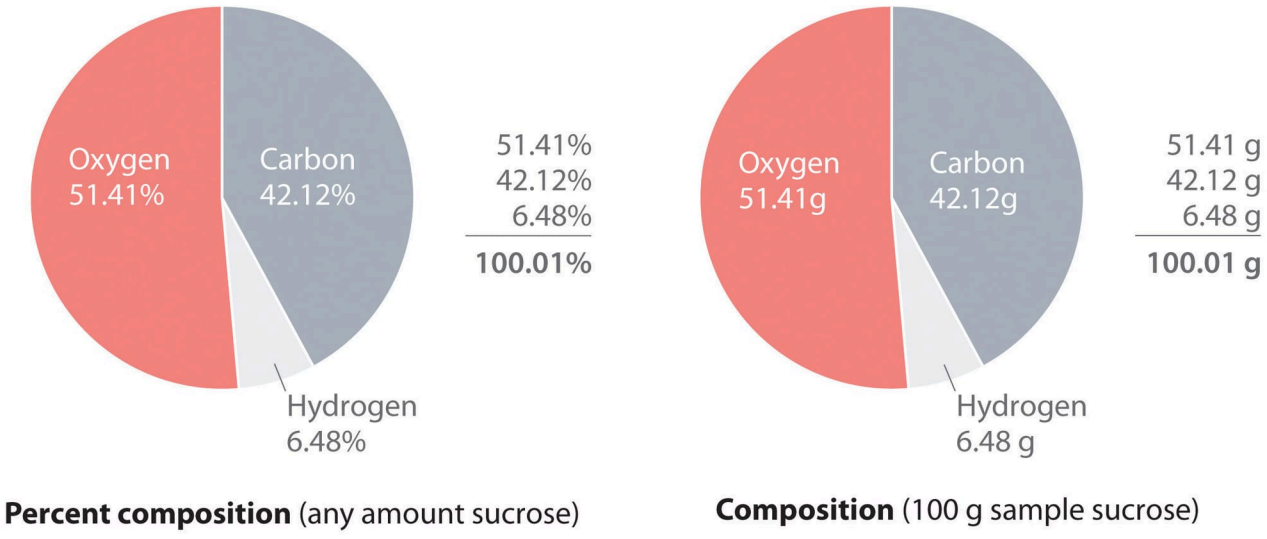
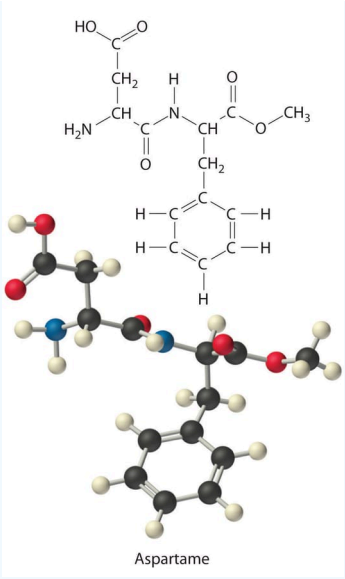


Figure 3.3.1: Percent and absolute composition of sucrose

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

Aspartame is the artificial sweetener sold as NutraSweet and Equal. Its molecular formula is $C_{14}H_{18}N_2O_5$.



Aspartame

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:

$$14\,C(14\,mol\,C)(12.011\,g/mol\,C) = 168.154\,g \tag{3.3.14}$$

$$18\,H(18\,mol\,H)(1.008\,g/mol\,H) = 18.114\,g \tag{3.3.15}$$

$$2\,N(2\,mol\,N)(14.007\,g/mol\,N) = 28.014\,g \tag{3.3.16}$$

$$+5\,O(5\,mol\,O)(15.999\,g/mol\,O) = 79.995\,g \tag{3.3.17}$$

$$C_{14}H_{18}N_2O_5 \text{molar mass of aspartame} = 294.277\,g/mol \tag{3.3.18}$$

Thus more than half the mass of 1 mol of aspartame (294.277 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:

$$mass\%\,C = \frac{168.154\,g\,C}{294.277\,g\,aspartame} \times 100 = 57.14\%C \tag{3.3.19}$$

$$mass\%\,H = \frac{18.114\,g\,H}{294.277\,g\,aspartame} \times 100 = 6.16\%H \tag{3.3.20}$$

$$mass\%\,N = \frac{28.014\,g\,N}{294.277\,g\,aspartame} \times 100 = 9.52\% \tag{3.3.21}$$

$$mass\%\,O = \frac{79.995\,g\,O}{294.277\,g\,aspartame} \times 100 = 27.18\% \tag{3.3.22}$$

As a check, we can add the percentages together:

$$57.14\% + 6.16\% + 9.52\% + 27.18\% = 100.00\% \tag{3.3.23}$$

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:

$$\text{mass of C} = 1.00\,g\,aspartame \times \frac{57.14\,g\,C}{100\,g\,aspartame} = 0.571\,g\,C \tag{3.3.24}$$

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: 52.93% aluminum; 47.08% oxygen; 1.92 g Al

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Percent Composition: https://youtu.be/HNS6lItns10

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.

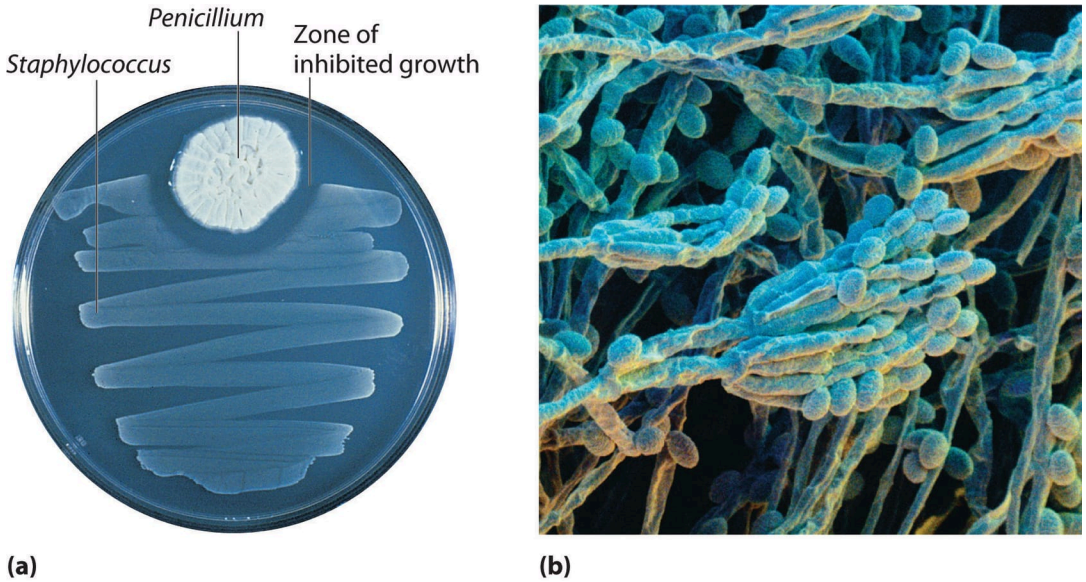


Figure 3.3.2 Penicillium. *(a) Penicillium mold is growing in a culture dish; the photo shows its effect on bacterial growth. (b) In this photomicrograph of Penicillium, its rod- and pencil-shaped branches are visible. The name comes from the Latin penicillus, meaning "paintbrush."*

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:

$$\frac{mass\,(g)}{molar\ mass\ (g/mol)} = (g)\left(\frac{mol}{g}\right) = mol \tag{3.3.25}$$

$$53.9\,g\,C\left(\frac{1\,mol\,C}{12.011\,g\,C}\right) = 4.49\,mol\,C \tag{3.3.26}$$

$$4.8\,g\,H\left(\frac{1\,mol\,H}{1.008 g\,H}\right) = 4.8\,mol\,H \tag{3.3.27}$$

$$7.9\,g\,N\left(\frac{1\,mol\,N}{14.007\,g\,N}\right) = 0.56\,mol\,N \tag{3.3.28}$$

$$9\,g\,S\left(\frac{1\,mol\,S}{32.065\,g\,S}\right) = 0.28\,mol\,S \tag{3.3.29}$$

$$6.5\,g\,Na\left(\frac{1\,mol\,Na}{22.990\,g\,Na}\right) = 0.28\,mol\,Na \tag{3.3.30}$$

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:

$$C: \frac{4.49}{0.28} = 16 \quad H: \frac{4.8}{0.28} = 17 \quad N: \frac{0.56}{0.28} = 2.0 \tag{3.3.31}$$

$$S: \frac{0.28}{0.28} = 1.0 \quad Na: \frac{0.28}{0.28} = 1.0 \quad O: \frac{1.12}{0.28} = 4.0 \tag{3.3.32}$$

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.

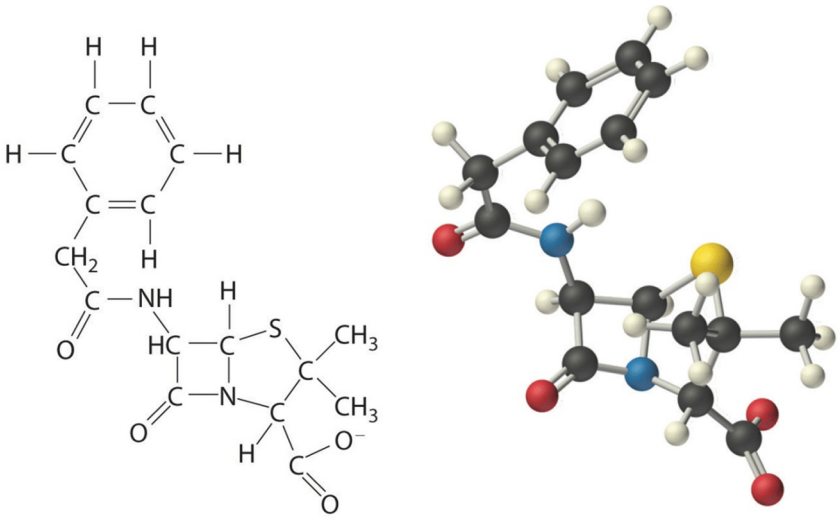


Figure 3.3.3 Structural Formula and Ball-and-Stick Model of the Anion of Penicillin G

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:

$$\text{moles Ca} = 38.77\,g\,Ca \times \frac{1\,mol\,Ca}{40.078\,g\,Ca} = 0.9674\,mol\,Ca \tag{3.3.33}$$

$$\text{moles P} = 19.97\,g\,P \times \frac{1\,mol\,P}{30.9738\,g\,P} = 0.6447\,mol\,Ca \tag{3.3.34}$$

$$\text{moles O} = 41.27\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 2.5800\,mol\,O \tag{3.3.35}$$

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:

$$P: \frac{0.6447\,mol\,P}{0.6447\,mol\,P} = 1.000 \quad Ca: \frac{0.9674}{0.6447} = 1.501 \quad O: \frac{2.5800}{0.6447} = 4.002 \tag{3.3.36}$$

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: Oklahoma City Bombing

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

$N_2H_4O_3$ is $NH_4^+NO_3^-$, written as NH_4NO_3

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Determining Empirical and Molecular Formulas from % Composition: https://youtu.be/E-MxBYw1TSI

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:

$$moles\,C = 39.68\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 3.304\,mol\,C \tag{3.3.37}$$

$$moles\,H = 6.58\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 6.53\,mol\,H \tag{3.3.38}$$

$$moles\,O = 53.79\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 3.362\,mol\,O \tag{3.3.39}$$

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:

$$C: \frac{3.304}{3.304} = 1.000 \quad H: \frac{6.53}{3.304} = 1.98 \quad O: \frac{3.362}{3.304} = 1.018 \tag{3.3.40}$$

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,

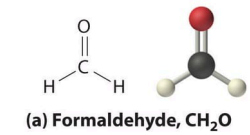
$$\text{formula mass of} CH_2O = \left[1\,mol C\left(\frac{12.011\,g}{1\,mol\,C}\right)\right] + \left[2\,mol\,H\left(\frac{1.0079\,g}{1\,mol\,H}\right)\right] + \left[1\,mole\,O\left(\frac{15.5994\,mol\,O}{1\,mol\,O}\right)\right] = 30.026g \tag{3.3.41}$$

This is much smaller than the observed molar mass of 180 g/mol.

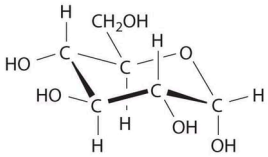
Second, determine the number of formula units per mole. For glucose, calculate the number of (CH_2O) units—that is, the n in $(CH_2O)_n$—by dividing the molar mass of glucose by the formula mass of CH_2O:

$$n = \frac{180\,g}{30.026\,g/CH_2O} = 5.99 \approx 6CH_2O\,\text{formula units} \tag{3.3.42}$$

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.



(a) Formaldehyde, CH_2O



(b) Glucose, $(CH_2O)_6$

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.

$$moles\,C = 49.18\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 4.095\,mol\,C \tag{3.3.43}$$

$$moles\,H = 5.39\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 5.35\,mol\,H \tag{3.3.44}$$

$$moles\,N = 28.65\,g\,N \times \frac{1\,mol\,N}{14.0067\,g\,N} = 2.045\,mol\,N \tag{3.3.45}$$

$$moles\,O = 16.68\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 1.043\,mol\,O \tag{3.3.46}$$

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:

$$O: \frac{1.043}{1.043} = 1.000 \quad C: \frac{4.095}{1.043} = 3.926 \quad H: \frac{5.35}{1.043} = 5.13 \quad N: \frac{2.045}{1.043} = 1.960 \tag{3.3.47}$$

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:

$$4C \quad (4\,atoms\,C)(12.011\,g/atom\,C) = 48.044\,g \tag{3.3.48}$$

$$5H \quad (5\,atoms\,H)(1.0079\,g/atom\,H) = 5.0395\,g \tag{3.3.49}$$

$$2N \quad (2\,atoms\,N)(14.0067\,g/atom\,N) = 28.0134\,g \tag{3.3.50}$$

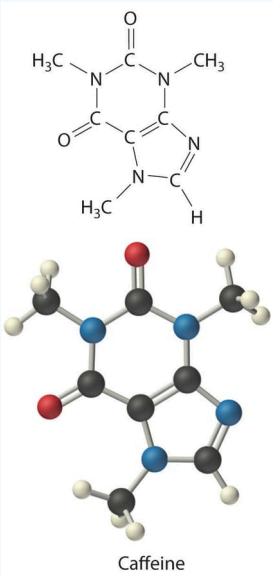
$$+1O \quad (1\,atom\,O)(15.9994\,g/atom\,O) = 15.9994\,g \tag{3.3.51}$$

$$C_4H_5N_2O \quad \text{formula mass of caffeine} = 97.096\,g \tag{3.3.52}$$

Dividing the measured molar mass of caffeine (196 g/mol) by the calculated formula mass gives

$$\frac{196g/mol}{97.096g/C_4H_5N_2O} = 2.02 \approx 2\, C_4H_5N_2O \,\text{empirical formula units} \tag{3.3.53}$$

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:

$$C_2Cl_2F_4 \tag{3.3.54}$$

Combustion Analysis

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 3.3.5 and a typical combustion analysis is illustrated in Example 3.3.4.

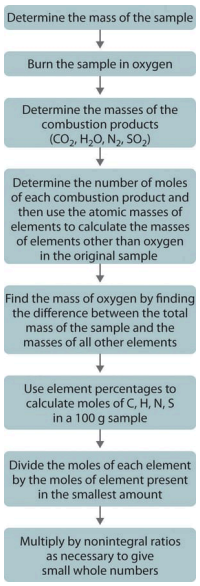


Figure 3.3.5: Steps for Obtaining an Empirical Formula from Combustion Analysis

Example 3.3.4

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:

$$mass\,of\,C = 69.00\,mg\,CO_2 \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,CO_2}{44.010\,g\,CO_2} \times \frac{1\,mol C}{1\,mol\,CO_2} \times \frac{12.011\,g}{1\,mol\,C} \tag{3.3.55}$$

$$= 1.883 \times 10^{-2}\,g\,C \tag{3.3.56}$$

$$mass\,of\,H = 11.30\,mg\,H_2O \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,H_2O}{18.015\,g\,H_2O} \times \frac{2\,mol H}{1\,mol\,H_2O} \times \frac{1.0079\,g}{1\,mol\,H} \tag{3.3.57}$$

$$= 1.264 \times 10^{-3}\,g\,H \tag{3.3.58}$$

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:

$$moles\,C = 1.883 \times 10^{-2}\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 1.568 \times 10^{-3}\,molC \tag{3.3.59}$$

$$moles\,H = 1.264 \times 10^{-3}\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 1.254 \times 10^{-3}\,molH \tag{3.3.60}$$

Dividing each number by the number of moles of the element present in the smaller amount gives

$$H: \frac{1.254 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.000 \;\; C: \frac{1.568 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.250 \tag{3.3.61}$$

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 molecular formula of naphthalene is $C_{10}H_8$, which is consistent with our results.

Exercise 3.3.4

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 molecular 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. The empirical formula is C_4H_5. (The molecular formula of xylene is actually C_8H_{10}.)
b. 33.81 mg of CO_2; 6.92 mg of H_2O

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

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3.4: Oxidation States: A Useful Tool in Describing Chemical Compounds

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, coherent, 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.

Note

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). The reaction is as follows:

$$Cu_2O(s) + H_2(g) \rightarrow 2Cu(s) + H_2O(g) \tag{3.4.1}$$

Oxidation and reduction reactions are now defined as reactions that exhibit a change in the oxidation states of one or more elements in the reactants, 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

$$4Al(s) + 3O_2 \rightarrow 2Al_2O_3(s) \tag{3.4.2}$$

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 superscript 0 emphasizes the oxidation state of the elements):

$$4Al^0 + 3O_2^0 \rightarrow 4Al^{3+} + 6O^{2-} \tag{3.4.3}$$

Equation 3.4.1 and Equation 3.4.2 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 3.4.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$electrons\,lost = 4\,Al\,atoms \times \frac{3\,e^-\,lost}{Al\,atom} = 12\,e^-\,lost \tag{3.4.4}$$

Label '3.4.4a' multiply defined

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 oxygen in air, is illustrated in Figure 3.4.1.

Note

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. Previosuly, 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 3.4.1), magnesium oxide (MgO), and calcium chloride ($CaCl_2$). In covalent compounds, in contrast, atoms share electrons. Oxidation states in covalent compounds are somewhat arbitrary, but they are useful bookkeeping devices to help you understand and predict many reactions.

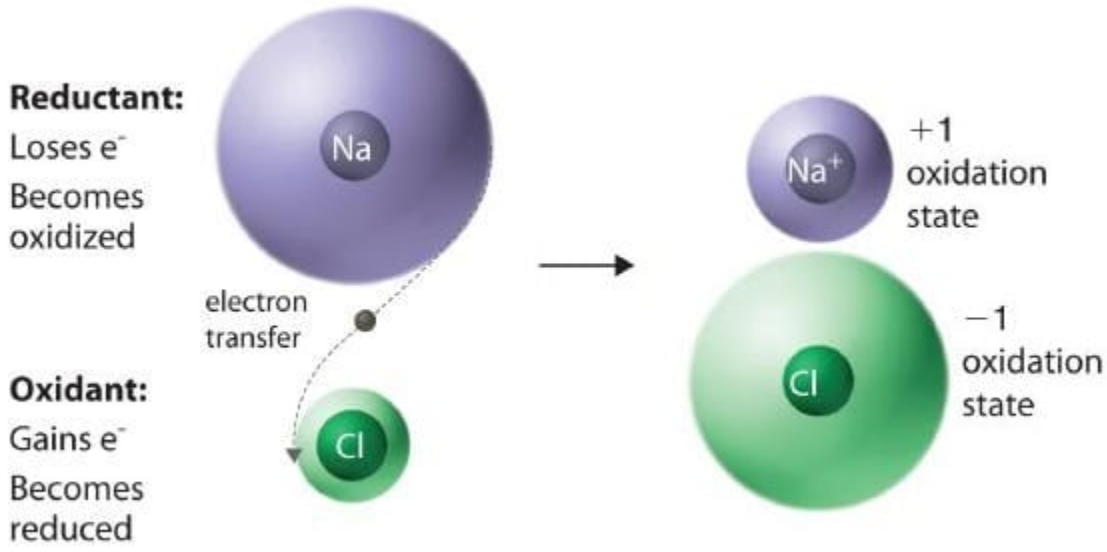


Figure 3.4.1: The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom. The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.

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 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 3.4.5 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:

$$\overset{+1}{Cu}_2\overset{-2}{O}(s) + \overset{0}{H}_2(g) \rightarrow 2\overset{0}{Cu}(s) + \overset{+1}{H}_2\overset{-2}{O}(g) \tag{3.4.5}$$

Assigning oxidation states allows us to see that there has been a net transfer of electrons from hydrogen (0 → +1) to copper (+1 → 0). So 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:

$$electrons\,lost = 2\,H\,atoms \times \frac{1\,e^-\,lost}{H\,atom} = 2\,e^-\,lost \tag{3.4.6}$$

$$electrons\,gained = 2\,Cu\,atoms \times \frac{1\,e^-\,gained}{Cu\,atom} = 2\,e^-\,gained \tag{3.4.7}$$

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 3.4.1

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

$$\overset{-3}{C}\overset{+1}{H_3}\overset{+3}{C}\overset{-2}{O_2}\overset{+1}{H} \tag{3.4.8}$$

Thus the sum of the oxidation states of the two carbon atoms is indeed zero.

Exercise 3.4.1

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. Ba, +2; F, −1
b. C, 0; H, +1; O, −2
c. K, +1; Cr, +6; O, −2
d. Cs, +1; O, −½
e. C, −3; H, +1; C, −1; H, +1; O, −2; H, +1

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 3.4.1). 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:

Label '3.4.5' multiply defined

In subsequent steps, $FeCl_2$ undergoes oxidation to form a reddish-brown precipitate of $Fe(OH)_3$.



Figure 3.4.2: 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

$$metal + acid \rightarrow salt + hydrogen \tag{3.4.9}$$

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:

$$Pb(s) + 2H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g) \tag{3.4.10}$$

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 3.4.8) and the reduction of silver salts by copper (Equation 3.4.9 and Figure 3.4.2):

$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s) \tag{3.4.11}$$

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s) \tag{3.4.12}$$

The reaction in Equation 3.4.8 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.



Figure used with permission of Wikipedia

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 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:

$$Zn(s) + Mg^{2+}(aq) \not\rightarrow Zn^{2+}(aq) + Mg(s) \tag{3.4.13}$$

$$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s) \tag{3.4.14}$$

Magnesium has a greater tendency to be oxidized than zinc does.

Pairwise reactions of this sort are the basis of the activity series (Figure 3.4.4), 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).

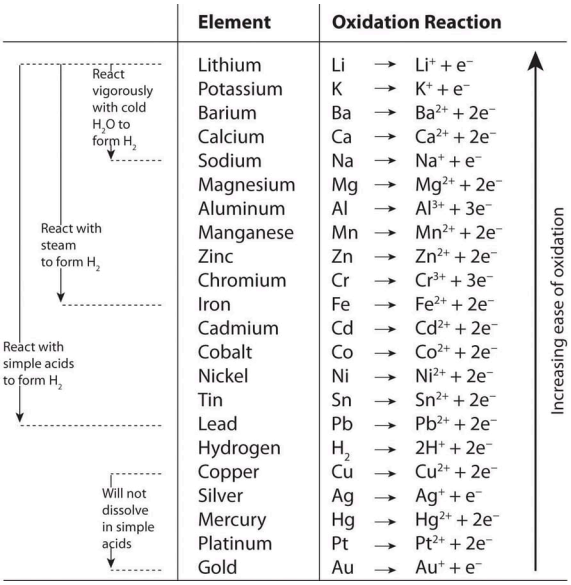


Figure 3.4.4: The Activity Series

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 3.4.4, 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 3.4.2 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions.

Example 3.4.2

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

1. A strip of aluminum foil is placed in an aqueous solution of silver nitrate.
2. A few drops of liquid mercury are added to an aqueous solution of lead(II) acetate.
3. 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 .3.4.4 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:

$$Al(s) + 3Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3Ag(s) \tag{3.4.15}$$

   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:

$$Pb(s) + 2H^{+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + H_2(g) \tag{3.4.16}$$

   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 3.4.2

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

1. A strip of chromium metal is placed in an aqueous solution of aluminum chloride.
2. A strip of zinc is placed in an aqueous solution of chromium(III) nitrate.
3. A piece of aluminum foil is dropped into a glass that contains vinegar (the active ingredient is acetic acid).

Answer

1. $no\ reaction$
2. $3Zn(s) + 2Cr^{3+}(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr(s)$
3. $2Al(s) + 6CH_3CO_2H(aq) \rightarrow 2Al^{3+}(aq) + 6CH_3CO_2^{-}(aq) + 3H_2(g)$

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 3.4.1), in which the overall reaction is separated into an oxidation equation and a reduction equation. **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 3.4.3), 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.

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3.5: Importance of Nomenclature

The primary function of chemical nomenclature is to ensure that a spoken or written chemical name leaves no ambiguity concerning which chemical compound the name refers to: each chemical name should refer to a single substance. A less important aim is to ensure that each substance has a single name (although a limited number of alternative names is acceptable in some cases). The form of nomenclature used depends on the audience to which it is addressed. As such, no single ***correct*** form exists, but rather there are different forms that are more or less appropriate in different circumstances. A common name will often suffice to identify a chemical compound in a particular set of circumstances. However, in a few specific circumstances (such as the construction of large indices), it becomes necessary to ensure that each compound has a unique name.

In discussing chemistry nomenclatures is it necessary to identify the type of compound including stoichiometry and type of constituent atoms. The first separation of importance is to distinguish between **inorganic** and **organic** compounds. Unfortunately, this separation is not always clear. even to experienced chemists. Historically (two centuries ago) the definitions were that inorganic compounds were synthesized by geological systems and organic compounds were found in biological systems. The modern definitions argues that organic compounds are any molecule containing carbon and by default this means that inorganic chemistry deals with molecules lacking carbon. The confusion arise when chemists that study carbon based materials like diamond or graphite, but that argument is beyond the scope of this text. The following sections presents the current nomenclature rules for inorganic and organic molecules.

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3.6: Names and Formulas of Inorganic Compounds

Learning Objectives

- To name ionic compounds.

The empirical and molecular formulas discussed in the preceding section are precise and informative, but they have some disadvantages. First, they are inconvenient for routine verbal communication. For example, saying "C-A-three-P-O-four-two" for $Ca_3(PO_4)_2$ is much more difficult than saying "calcium phosphate." In addition, many compounds have the same empirical and molecular formulas but different arrangements of atoms, which differences result in very different chemical and physical properties. In such cases, it is necessary for the compounds to have different names that distinguish among the possible arrangements.

Many compounds, particularly those that have been known for a relatively long time, have more than one name: a common name (sometimes several), and a systematic name, which is the name assigned by adhering to specific rules. Like the names of most elements, the common names of chemical compounds generally have historical origins, although they often appear to be unrelated to the compounds of interest. For example, the systematic name for KNO_3 is potassium nitrate, but its common name is *saltpeter*.

In this text, a systematic nomenclature is used to assign meaningful names to the millions of known substances. Unfortunately, some chemicals that are widely used in commerce and industry are still known almost exclusively by their common names; in such cases, familiarity with the common name as well as the systematic one is required. The objective of this and the next two sections is to teach how to write the formula for a simple inorganic compound from its name—and vice versa—and introduce some frequently-encountered common names.

Binary ionic compounds contain only two elements. The procedure for naming such compounds is outlined in Figure 3.6.1 and uses the following steps:

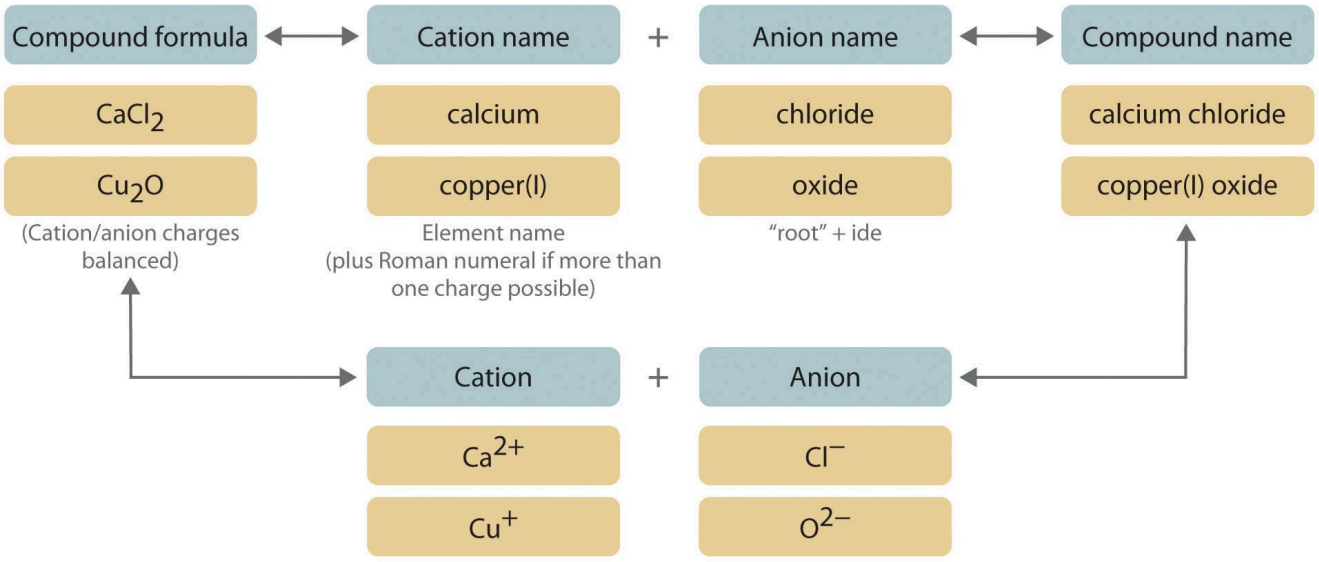


Figure 3.6.1: Naming an Ionic Compound

1. Place the ions in their proper order: cation and then anion.

2. Name the cation.

    a. **Metals that form only one cation**. As noted previosuly, these metals are usually in Groups 1–3, 12, and 13. The name of the cation of a metal that forms only one cation is the same as the name of the metal (with the word ion added if the cation

is by itself). For example, Na^+ is the sodium ion, Ca^{2+} is the calcium ion, and Al^{3+} is the aluminum ion.

b. **Metals that form more than one cation**. As shown in Figure 3.6.2, many metals can form more than one cation. This behavior is observed for most transition metals, many actinides, and the heaviest elements of Groups 13–15. In such cases, the positive charge on the metal is indicated by a roman numeral in parentheses immediately following the name of the metal. Thus Cu^+ is copper(I) (read as "copper one"), Fe^{2+} is iron(II), Fe^{3+} is iron(III), Sn^{2+} is tin(II), and Sn^{4+} is tin(IV).

An older system of nomenclature for such cations is still widely used, however. The name of the cation with the higher charge is formed from the root of the element's Latin name with the suffix -ic attached, and the name of the cation with the lower charge has the same root with the suffix -ous. The names of Fe^{3+}, Fe^{2+}, Sn^{4+}, and Sn^{2+} are therefore ferric, ferrous, stannic, and stannous, respectively. Even though this text uses the systematic names with roman numerals, it is important to recognize these common names because they are still often used. For example, on the label of dental fluoride rinse, the compound chemists call tin(II) fluoride is usually listed as stannous fluoride.

Some examples of metals that form more than one cation are listed in Table 3.6.1, along with the names of the ions. Note that the simple Hg^+ cation does not occur in chemical compounds. Instead, all compounds of mercury(I) contain a dimeric cation, Hg_2^{2+}, in which the two Hg atoms are bonded together.

Table 3.6.1: Common Cations of Metals That Form More Than One Ion

Cation	Systematic Name	Common Name	Cation	Systematic Name	Common Name
Co^{2+}	cobalt(II)	cobaltous*	Pb^{4+}	lead(IV)	plumbic*
Co^{3+}	cobalt(III)	cobaltic*	Pb^{2+}	lead(II)	plumbous*
Cr^{2+}	chromium(II)	chromous	Cu^{2+}	copper(II)	cupric
Cr^{3+}	chromium(III)	chromic	Cu^+	copper(I)	cuprous
Fe^{2+}	iron(II)	ferrous	Sn^{4+}	tin(IV)	stannic
Fe^{3+}	iron(III)	ferric	Sn^{2+}	tin(II)	stannous
Mn^{2+}	manganese(II)	manganous*	Hg^{2+}	mercury(II)	mercuric
Mn^{3+}	manganese(III)	manganic*	Hg_2^{2+}	mercury(I)	mercurous†
*** Not widely used.**					
†The isolated mercury(I) ion exists only as the gaseous ion.					

c. **Polyatomic cations**. The names of the common polyatomic cations that are relatively important in ionic compounds (such as, the ammonium ion) are in Table 2.4

3. Name the anion.

a. **Monatomic anions**. Monatomic anions are named by adding the suffix -ide to the root of the name of the parent element; thus, Cl^- is chloride, O^{2-} is oxide, P^{3-} is phosphide, N^{3-} is nitride (also called azide), and C^{4-} is carbide. Because the charges on these ions can be predicted from their position in the periodic table, it is not necessary to specify the charge in the name. Examples of monatomic anions are in Table 2.2

b. **Polyatomic anions**. Polyatomic anions typically have common names that must be memorized; some examples are in Table 2.4. Polyatomic anions that contain a single metal or nonmetal atom plus one or more oxygen atoms are called oxoanions (or oxyanions). In cases where only two oxoanions are known for an element, the name of the oxoanion with more oxygen atoms ends in -ate, and the name of the oxoanion with fewer oxygen atoms ends in -ite. For example, NO_3^- is nitrate and NO_2^- is nitrite.

The halogens and some of the transition metals form more extensive series of oxoanions with as many as four members. In the names of these oxoanions, the prefix per- is used to identify the oxoanion with the most oxygen (so that ClO_4^- is

perchlorate and ClO_3^- is chlorate), and the prefix hypo- is used to identify the anion with the fewest oxygen (ClO_2^- is chlorite and ClO^- is hypochlorite). The relationship between the names of oxoanions and the number of oxygen atoms present is diagrammed in Figure 3.6.3 "The Relationship between the Names of Oxoanions and the Number of Oxygen Atoms Present." Differentiating the oxoanions in such a series is no trivial matter; for example, the hypochlorite ion is the active ingredient in laundry bleach and swimming pool disinfectant, but compounds that contain the perchlorate ion can explode if they come into contact with organic substances.

4. Write the name of the compound as the name of the cation followed by the name of the anion.

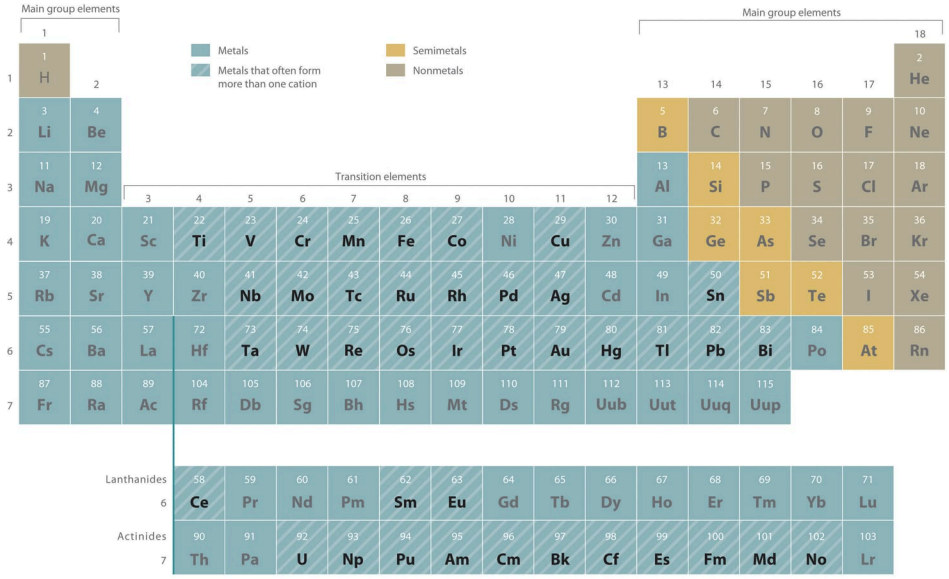


Figure 3.6.2: Metals That Form More Than One Cation and Their Locations in the Periodic Table

It is not necessary to indicate the number of cations or anions present per formula unit in the name of an ionic compound because this information is implied by the charges on the ions. The charge of the ions must be considered when writing the formula for an ionic compound from its name, however. Because the charge on the chloride ion is –1 and the charge on the calcium ion is +2, for example, consistent with their positions in the periodic table, arithmetic indicates that calcium chloride must contain twice as many chloride ions as calcium ions to maintain electrical neutrality. Thus, the formula is $CaCl_2$. Similarly, calcium phosphate must be $Ca_3(PO_4)_2$ because the cation and the anion have charges of +2 and –3, respectively. The best way to learn how to name ionic compounds is to work through a few examples, referring to Figure 3.6.1, Table 2.2, Table 2.4, and Table 3.6.1 as needed.

With only a few exceptions, these metals are usually transition metals or actinides.

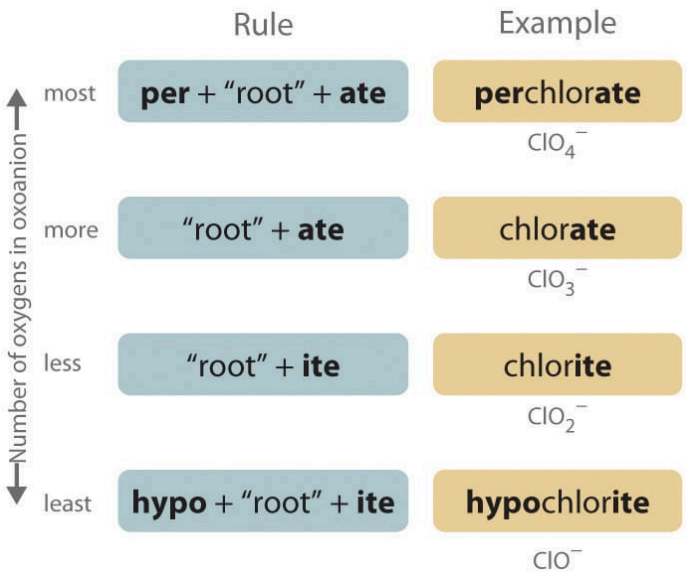


Figure 3.6.3: The Relationship between the Names of Oxoanions and the Number of Oxygen Atoms Present

Note

Cations are always named before anions.

Most transition metals, many actinides, and the heaviest elements of groups 13–15 can form more than one cation.

Example 3.6.1

Write the systematic name (and the common name if applicable) for each ionic compound.

a. LiCl
b. $MgSO_4$
c. $(NH_4)_3PO_4$
d. Cu_2O

Given: empirical formula

Asked for: name

Strategy:

A If only one charge is possible for the cation, give its name, consulting Table 2.2 or Table 2.4 if necessary. If the cation can have more than one charge (Table 3.6.1), specify the charge using roman numerals.

B If the anion does not contain oxygen, name it according to step 3a, using Table 2.2 and Table 2.4 if necessary. For polyatomic anions that contain oxygen, use Table 2.4 and the appropriate prefix and suffix listed in step 3b.

C Beginning with the cation, write the name of the compound.

Solution:

a. **A B** Lithium is in group 1, so we know that it forms only the Li^+ cation, which is the lithium ion. Similarly, chlorine is in group 7, so it forms the Cl^- anion, which is the chloride ion. **C** Because we begin with the name of the cation, the name of this compound is lithium chloride, which is used medically as an antidepressant drug.

b. **A B** The cation is the magnesium ion, and the anion, which contains oxygen, is sulfate. **C** Because we list the cation first, the name of this compound is magnesium sulfate. **A** hydrated form of magnesium sulfate ($MgSO_4 \cdot 7H_2O$) is sold in drugstores as Epsom salts, a harsh but effective laxative.

c. **A B** The cation is the ammonium ion (from Table 2.4), and the anion is phosphate. C The compound is therefore ammonium phosphate, which is widely used as a fertilizer. It is not necessary to specify that the formula unit contains three ammonium ions because three are required to balance the negative charge on phosphate.

d. **A B** The cation is a transition metal that often forms more than one cation (Table 3.6.1). We must therefore specify the positive charge on the cation in the name: copper(I) or, according to the older system, cuprous. The anion is oxide. C The name of this compound is copper(I) oxide or, in the older system, cuprous oxide. Copper(I) oxide is used as a red glaze on ceramics and in antifouling paints to prevent organisms from growing on the bottoms of boats.



Cu_2O. *The bottom of a boat is protected with a red antifouling paint containing copper(I) oxide, Cu_2O.*

Exercise 3.6.1

Exercise

Write the systematic name (and the common name if applicable) for each ionic compound.

a. $CuCl_2$
b. $MgCO_3$
c. $FePO_4$

Answer:

a. copper(II) chloride (or cupric chloride)
b. magnesium carbonate
c. iron(III) phosphate (or ferric phosphate)

Example 3.6.2

Write the formula for each compound.

a. calcium dihydrogen phosphate
b. aluminum sulfate
c. chromium(III) oxide

Given: systematic name

Asked for: formula

Strategy:

A Identify the cation and its charge using the location of the element in the periodic table and Table 2.2 and form cations with different charges, use the appropriate roman numeral or suffix to indicate its charge.

B Identify the anion using Table 2.2 and Table 2.4. Beginning with the cation, write the compound's formula and then determine the number of cations and anions needed to achieve electrical neutrality.

Solution:

a. **A** Calcium is in group 2, so it forms only the Ca^{2+} ion. **B** Dihydrogen phosphate is the H_2PO_4– ion (Table 2.4). Two $H_2PO_4^-$ ions are needed to balance the positive charge on Ca^{2+}, to give $Ca(H_2PO_4)_2$. A hydrate of calcium dihydrogen phosphate, $Ca(H_2PO_4)_2{\cdot}H_2O$, is the active ingredient in baking powder.

b. **A** Aluminum, near the top of group 13 in the periodic table, forms only one cation, Al^{3+} (Figure 3.6.2 "Metals That Form More Than One Cation and Their Locations in the Periodic Table"). B Sulfate is SO_4^{2-} (Table 2.4). To balance the electrical charges, we need two Al^{3+} cations and three SO_4^{2-} anions, giving $Al_2(SO_4)_3$. Aluminum sulfate is used to tan leather and purify drinking water.

c. **A** Because chromium is a transition metal, it can form cations with different charges. The roman numeral tells us that the positive charge in this case is +3, so the cation is Cr^{3+}. B Oxide is O^{2-}. Thus two cations (Cr^{3+}) and three anions (O^{2-}) are required to give an electrically neutral compound, Cr_2O_3. This compound is a common green pigment that has many uses, including camouflage coatings.



Cr_2O_3. *Chromium(III) oxide (Cr_2O_3) is a common pigment in dark green paints, such as camouflage paint.*

Exercise 3.6.2

Write the formula for each compound.

a. barium chloride
b. sodium carbonate
c. iron(III) hydroxide

Answer:

a. $BaCl_2$
b. Na_2CO_3
c. $Fe(OH)_3$

Summary

- There is a systematic method used to name ionic compounds.

Ionic compounds are named according to systematic procedures, although common names are widely used. Systematic nomenclature enables chemists to write the structure of any compound from its name and vice versa. Ionic compounds are named by writing the cation first, followed by the anion. If a metal can form cations with more than one charge, the charge is indicated by roman numerals in parentheses following the name of the metal. Oxoanions are polyatomic anions that contain a single metal or nonmetal atom and one or more oxygen atoms.

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 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 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 C_2H_5, but it contains two C_2H_5 formula units, giving a molecular formula of 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 Na^+ and 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 Mg^{2+} and Cl^-, for example, two Cl^- ions are needed to balance the two positive charges on each Mg^{2+} ion, giving an empirical formula of $MgCl_2$. Similarly, the formula for the ionic compound that contains Na^+ and O^{2-} ions is Na_2O.

Note

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

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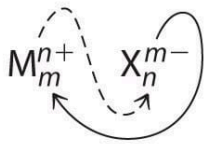
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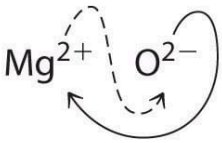
Binary Ionic Compounds

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 $MgCl_2$, 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 Mg^{2+} and O^{2-}. Using the absolute values of the charges on the ions as subscripts gives the formula 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 3.6.1

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

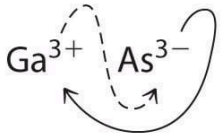
Strategy:

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.

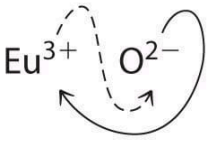
Solution

a. **B** Using the absolute values of the charges on the ions as the subscripts gives Ga3As3:



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.

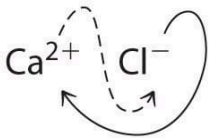
b. **B** Because Eu^{3+} has a charge of +3 and O^{2-} has a charge of −2, a 1:1 compound would have a net charge of +1. We must therefore find multiples of the charges that cancel. We cross charges, using the absolute value of the charge on one ion as the subscript for the other ion:



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 3.6.1

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. Li_3N
b. Al_2O_3
c. Li_2O

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 3.6.1.

Table 3.6.1: 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

Formula	Name of Ion	Formula	Name of Ion
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 3.6.2

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 3.6.1 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 3.6.2

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

Answer:

a. $Ca(H_2PO_4)_2$: calcium dihydrogen phosphate is one of the ingredients in baking powder.
b. $NaHCO_3$: sodium bicarbonate is found in antacids and baking powder; in pure form, it is sold as baking soda.
c. $(NH_4)_2SO_4$: ammonium sulfate is a common source of nitrogen in fertilizers.

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Polyatomics: https://youtu.be/kTSPkzDcntA

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 $CuSO_4{\cdot}5H_2O$. When heated, all five water molecules are lost, giving a white solid with the empirical formula $CuSO_4$.



Figure 3.6.1: 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, $CaSO_4 \cdot ½H2O$ is plaster of Paris, which was often used to make sturdy casts for broken arms or legs, whereas $CaSO_4 \cdot 2H_2O$ 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 $CaSO_4 \cdot 2H_2O$. Similar processes are used in the setting of cement and concrete.

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 3.6.2 consists of the following steps:

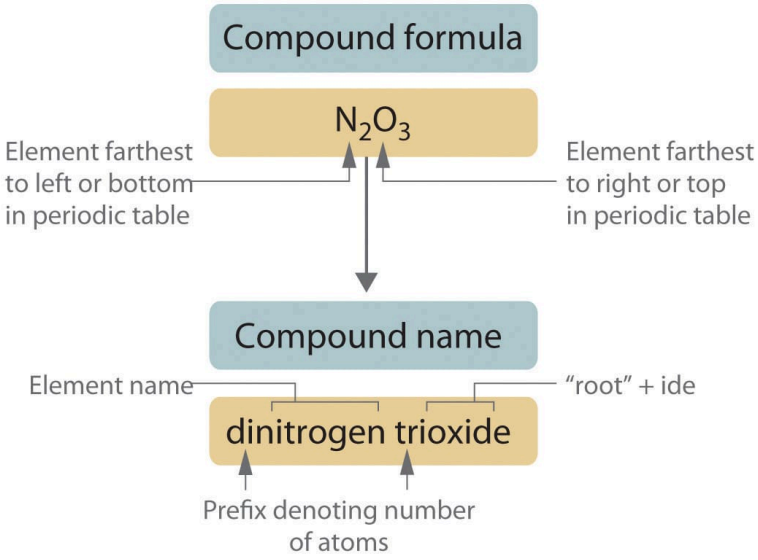


Figure 3.6.2 Naming a Covalent Inorganic Compound

1. Place the elements in their proper order.
    1. 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.
    2. 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 3.6.2). 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 3.6.2: 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

*trio*xide, 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.

Note

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 3.6.3

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 3.6.2 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 3.6.2). 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 3.6.2 "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 3.6.3

Write the name of each binary covalent compound.

a. IF_7
b. N_2O_5
c. OF_2

Answer

a. iodine heptafluoride
b. dinitrogen pentoxide
c. oxygen difluoride

Example 3.6.4

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 3.6.2 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 3.6.4

Write the formula for each binary covalent compound.

a. silicon tetrachloride
b. disulfur decafluoride

Answer

a. $SiCl_4$
b. S_2F_{10}

The structures of some of the compounds in Examples 3.6.3 and 3.6.4 are shown in Figure 3.6.2 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.

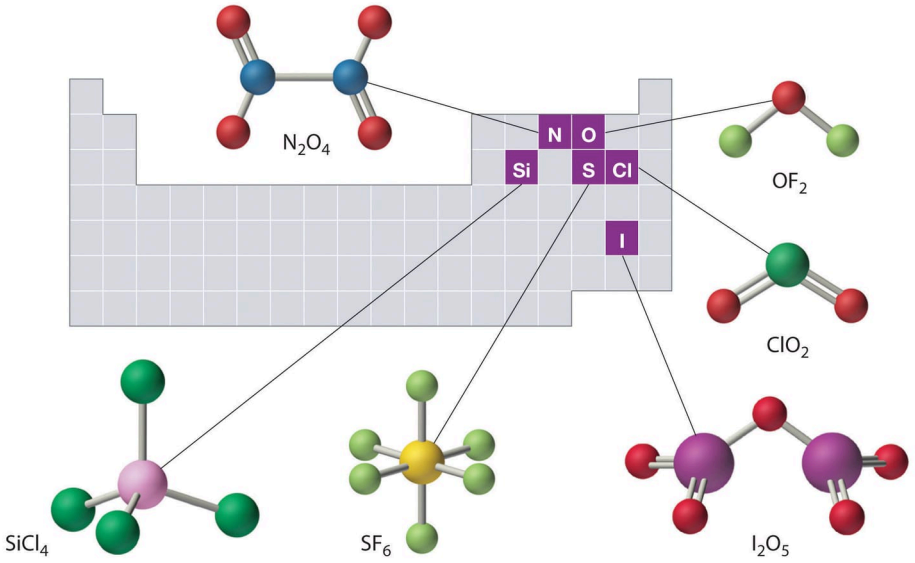


Figure 3.6.2 The Structures of Some Covalent Inorganic Compounds and the Locations of the "Central Atoms" in the Periodic Table. The compositions and structures of covalent inorganic compounds are not random and can be predicted from the locations of the component atoms in the periodic table.

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Nomenclature of Nonmetals: https://youtu.be/VgHCrtpDWJk

The Learning Objective of this Module is to identify and name some common acids and bases.

For our purposes at this point in the text, we can define an acid as 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. We can define bases as compounds that produce hydroxide ions (OH^-) and a cation when dissolved in water, thus forming a basic solution. Solutions that are neither basic nor acidic are neutral. We will discuss the chemistry of acids and bases in more detail later, but in this section we describe the nomenclature of common acids and identify some important bases so that you can recognize them in future discussions. Pure acids and bases and their concentrated aqueous solutions are commonly encountered in the laboratory. They are usually highly corrosive, so they must be handled with care.

Acids

The names of acids differentiate between (1) acids in which the H^+ ion is attached to an oxygen atom of a polyatomic anion (these are called oxoacids, or occasionally oxyacids) and (2) acids in which the H^+ ion is attached to some other element. In the latter case, the name of the acid begins with hydro- and ends in -ic, with the root of the name of the other element or ion in between. Recall that the name of the anion derived from this kind of acid always ends in -ide. Thus hydrogen chloride (HCl) gas dissolves in water to form hydrochloric acid (which contains H^+ and Cl^- ions), hydrogen cyanide (HCN) gas forms hydrocyanic acid (which contains H^+ and CN^- ions), and so forth (Table 3.6.3). Examples of this kind of acid are commonly encountered and very important. For instance, your stomach contains a dilute solution of hydrochloric acid to help digest food. When the mechanisms that prevent the stomach from digesting itself malfunction, the acid destroys the lining of the stomach and an ulcer forms.

Note

Acids are distinguished by whether the H^+ ion is attached to an oxygen atom of a polyatomic anion or some other element.

Table 3.6.3: Some Common Acids That Do Not Contain Oxygen

Formula	Name in Aqueous Solution	Name of Gaseous Species
HF	hydrofluoric acid	hydrogen fluoride
HCl	hydrochloric acid	hydrogen chloride
HBr	hydrobromic acid	hydrogen bromide
HI	hydroiodic acid	hydrogen iodide
HCN	hydrocyanic acid	hydrogen cyanide
H_2S	hydrosulfuric acid	hydrogen sulfide

If an acid contains one or more H^+ ions attached to oxygen, it is a derivative of one of the common oxoanions, such as sulfate (SO_4^{2-}) or nitrate (NO_3^-). These acids contain as many H^+ ions as are necessary to balance the negative charge on the anion, resulting in a neutral species such as H_2SO_4 and HNO_3.

The names of acids are derived from the names of anions according to the following rules:

1. **If the name of the anion ends in -ate, then the name of the acid ends in** -ic. For example, because NO_3^- is the nitrate ion, HNO_3 is nitric acid. Similarly, ClO_4^- is the perchlorate ion, so $HClO_4$ is perchloric acid. Two important acids are sulfuric acid (H_2SO_4) from the sulfate ion (SO_4^{2-}) and phosphoric acid (H_3PO_4) from the phosphate ion (PO_4^{3-}). These two names use a slight variant of the root of the anion name: sulfate becomes sulfuric and phosphate becomes phosphoric.
2. **If the name of the anion ends in -ite, then the name of the acid ends in** -ous. For example, OCl^- is the hypochlorite ion, and HOCl is hypochlorous acid; NO_2^- is the nitrite ion, and HNO_2 is nitrous acid; and SO_3^{2-} is the sulfite ion, and H_2SO_3 is sulfurous acid. The same roots are used whether the acid name ends in -ic or -ous; thus, sulfite becomes sulfurous.

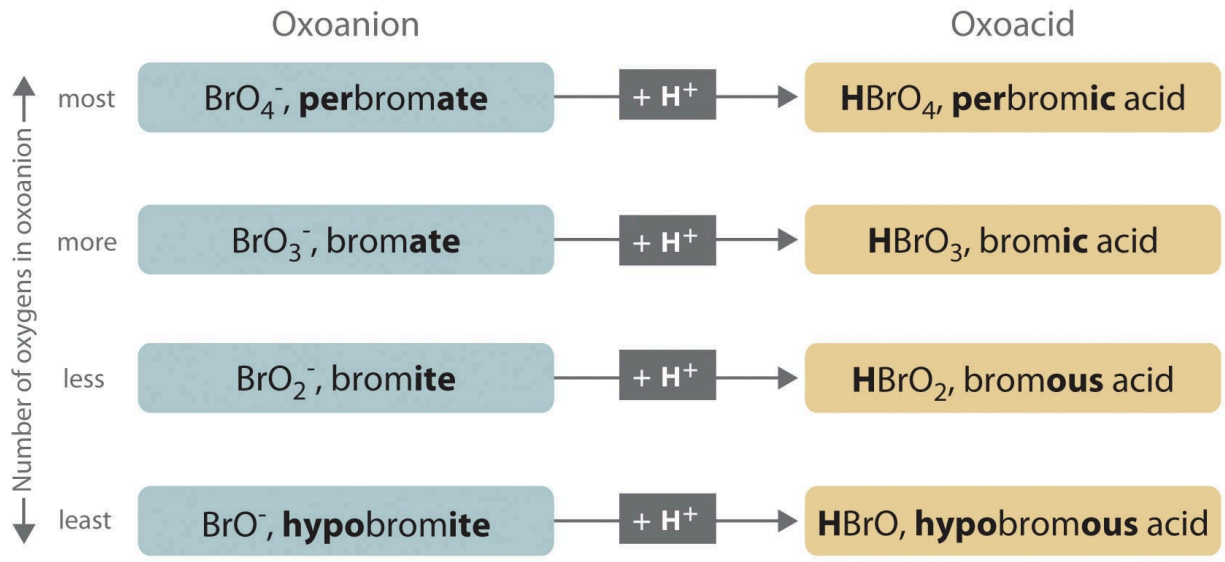


Figure 3.6.3: The Relationship between the Names of the Oxoacids and the Names of the Parent Oxoanions

The relationship between the names of the oxoacids and the parent oxoanions is illustrated in Figure 3.6.3, and some common oxoacids are in Table 3.6.4.

Table 3.6.4: Some Common Oxoacids

Formula	Name
HNO_2	nitrous acid
HNO_3	nitric acid
H_2SO_3	sulfurous acid
H_2SO_4	sulfuric acid
H_3PO_4	phosphoric acid
H_2CO_3	carbonic acid
$HClO$	hypochlorous acid
$HClO_2$	chlorous acid
$HClO_3$	chloric acid
$HClO_4$	perchloric acid

Example 3.6.5

Name and give the formula for each acid.

a. the acid formed by adding a proton to the hypobromite ion (OBr^-)
b. the acid formed by adding two protons to the selenate ion (SeO_4^{2-})

Given: anion

Asked for: parent acid

Strategy:

Refer to Table 3.6.3 and Table 3.6.4 to find the name of the acid. If the acid is not listed, use the guidelines given previously.

Solution:

Neither species is listed in Table 3.6.3 or Table 3.6.4, so we must use the information given previously to derive the name of the acid from the name of the polyatomic anion.

a. The anion name, hypobromite, ends in -ite, so the name of the parent acid ends in -ous. The acid is therefore hypobromous acid (HOBr).
b. Selenate ends in -ate, so the name of the parent acid ends in -ic. The acid is therefore selenic acid (H_2SeO_4).

Exercise 3.6.5

Name and give the formula for each acid.

a. the acid formed by adding a proton to the perbromate ion (BrO_4^-)
b. the acid formed by adding three protons to the arsenite ion (AsO_3^{3-})

Answer:

a. perbromic acid; $HBrO_4$
b. arsenous acid; H_3AsO_3

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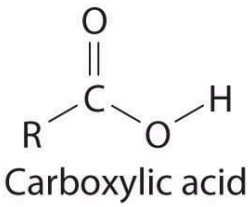
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Nomenclature of Acids: https://youtu.be/in46UUzmSO4

Organic Acids

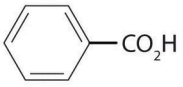
Many organic compounds contain the carbonyl group, in which there is a carbon–oxygen double bond. In carboxylic acids, an –OH group is covalently bonded to the carbon atom of the carbonyl group. Their general formula is RCO_2H, sometimes written as RCOOH:



Carboxylic acid

where R can be an alkyl group, an aryl group, or a hydrogen atom. The simplest example, HCO_2H, is formic acid, so called because it is found in the secretions of stinging ants (from the Latin *formica*, meaning "ant"). Another example is acetic acid (CH_3CO_2H), which is found in vinegar. Like many acids, carboxylic acids tend to have sharp odors. For example, butyric acid ($CH_3CH_2CH_2CO_2H$), is responsible for the smell of rancid butter, and the characteristic odor of sour milk and vomit is due to lactic acid [$CH_3CH(OH)CO_2H$]. Some common carboxylic acids are shown in Table 3.6.5.

Table 3.6.5*: Some Common Carboxylic Acids*

Formula (Structure)	Name	Uses
HCO_2H	formic acid	tanning, dyeing
CH_3CO_2H	acetic acid	vinegar, food preservative
$CH_3CH_2CO_2H$	propionic acid	food preservative
$CH_3CH_2CH_2CO_2H$	butyric acid	varnishes
$C_6H_5CO_2H$ 	benzoic acid	food preservative, dyeing

Although carboxylic acids are covalent compounds, when they dissolve in water, they dissociate to produce H^+ ions (just like any other acid) and RCO_2^- ions. Note that only the hydrogen attached to the oxygen atom of the CO_2 group dissociates to form an

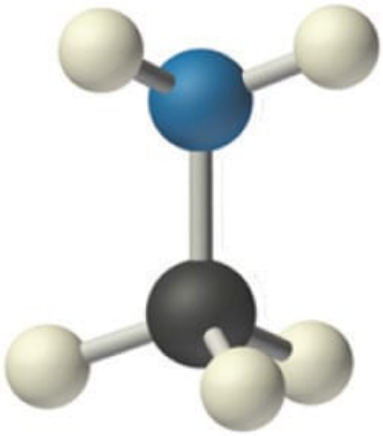
H^+ ion. In contrast, the hydrogen atom attached to the oxygen atom of an alcohol does not dissociate to form an H^+ ion when an alcohol is dissolved in water. The reasons for the difference in behavior between carboxylic acids and alcohols will be discussed in Chapter 8.

Note

Only the hydrogen attached to the oxygen atom of the CO_2 group dissociates to form an H^+ ion.

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.



Methylamine

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 NH3 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.

Note

Metal hydroxides (MOH) yield OH^- ions and are bases, alcohols (ROH) do not yield OH^- or H^+ ions and are neutral, and carboxylic acids (RCO_2H) yield H^+ ions and are acids.

Summary

Common acids and the polyatomic anions derived from them have their own names and rules for nomenclature. The nomenclature of acids differentiates between oxoacids, in which the H^+ ion is attached to an oxygen atom of a polyatomic ion, and acids in which the H^+ ion is attached to another element. Carboxylic acids are an important class of organic acids. Ammonia is an important base, as are its organic derivatives, the amines.

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.

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3.7: Names of Formulas of Organic Compounds

Learning Objectives

- Explain the following laws within the Ideal Gas Law:
  - Avogadro's law of gases

Hydrocarbons

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 s*aturated* hydrocarbons, whereas hydrocarbons that contain multiple bonds (alkenes, alkynes, and aromatics) are *unsaturated*.

Alkanes

The simplest alkane is methane (CH_4), a colorless, odorless gas that is the major component of natural gas. In larger alkanes whose carbon atoms are joined in an unbranched chain (*straight-chain alkanes*), each carbon atom is bonded to at most two other carbon atoms. The structures of two simple alkanes are shown in Figure $3.7.1$, and the names and condensed structural formulas for the first 10 straight-chain alkanes are in Table $3.7.1$. The names of all alkanes end in *-ane*, and their boiling points increase as the number of carbon atoms increases.

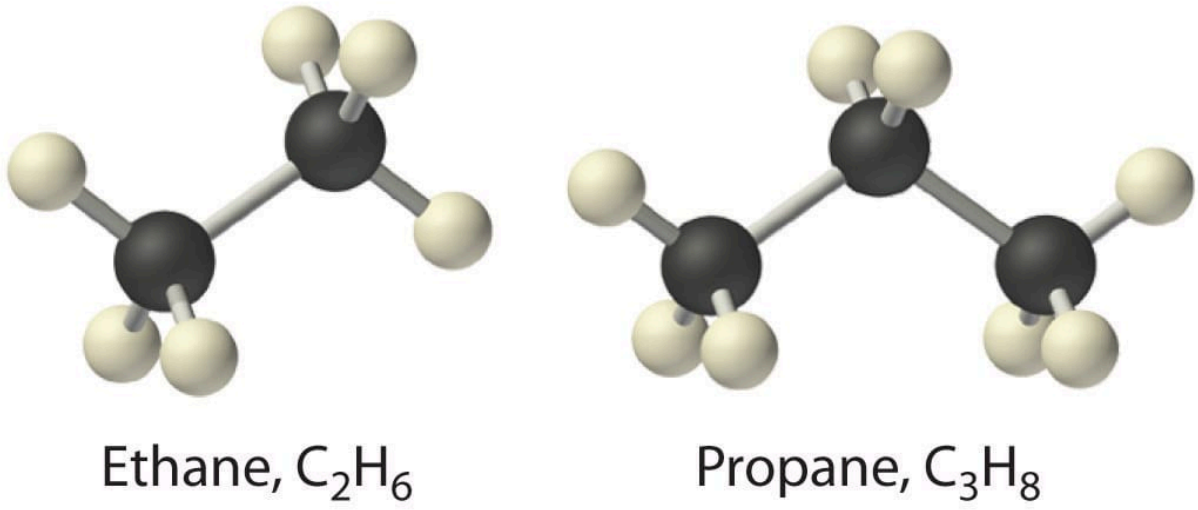
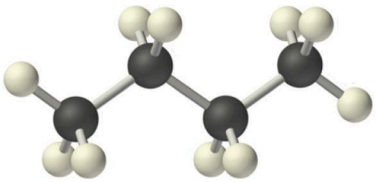


Figure $3.7.1$: Straight-Chain Alkanes with Two and Three Carbon Atoms

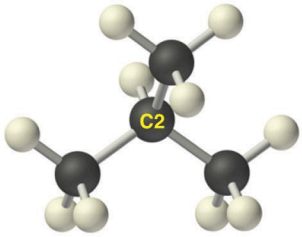
Table 3.7.1: The First 10 Straight-Chain Alkanes

Name	Number of Carbon Atoms	Molecular Formula	Condensed Structural Formula	Boiling Point (°C)	Uses
methane	1	CH_4	CH_4	–162	natural gas constituent
ethane	2	C_2H_6	CH_3CH_3	–89	natural gas constituent
propane	3	C_3H_8	$CH_3CH_2CH_3$	–42	bottled gas
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$	0	lighters, bottled gas
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	36	solvent, gasoline
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	69	solvent, gasoline
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	98	solvent, gasoline
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	126	gasoline
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	151	gasoline
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	174	kerosene

Alkanes with four or more carbon atoms can have more than one arrangement of atoms. The carbon atoms can form a single unbranched chain, or the primary chain of carbon atoms can have one or more shorter chains that form branches. For example, butane (C_4H_{10}) has two possible structures. *Normal* butane (usually called *n*-butane) is $CH_3CH_2CH_2CH_3$, in which the carbon atoms form a single unbranched chain. In contrast, the condensed structural formula for *isobutane* is $(CH_3)_2CHCH_3$, in which the primary chain of three carbon atoms has a one-carbon chain branching at the central carbon. Three-dimensional representations of both structures are as follows:

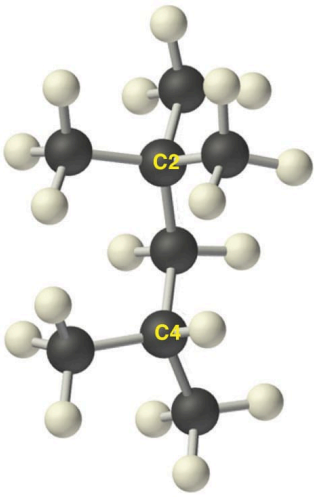


n-Butane, C_4H_{10}



Isobutane (2-methylpropane), C_4H_{10}

The systematic names for branched hydrocarbons use the lowest possible number to indicate the position of the branch along the longest straight carbon chain in the structure. Thus the systematic name for isobutane is 2-methylpropane, which indicates that a methyl group (a branch consisting of $-CH_3$) is attached to the second carbon of a propane molecule. Similarly, Section 2.6 states that one of the major components of gasoline is commonly called isooctane; its structure is as follows:



Isooctane (2,2,4-trimethylpentane)

The compound has a chain of five carbon atoms, so it is a derivative of pentane. There are two methyl group branches at one carbon atom and one methyl group at another. Using the lowest possible numbers for the branches gives 2,2,4-trimethylpentane for the systematic name of this compound.

Alkenes

The simplest alkenes are *ethylene*, C_2H_4 or $CH_2{=}CH_2$, and *propylene*, C_3H_6 or $CH_3CH{=}CH_2$ (part (a) in Figure 3.7.2). The names of alkenes that have more than three carbon atoms use the same stems as the names of the alkanes (Table 3.7.1 "The First 10 Straight-Chain Alkanes") but end in *-ene* instead of *-ane*.

As with alkanes, more than one structure is possible for alkenes with four or more carbon atoms. For example, an alkene with four carbon atoms has three possible structures. One is $CH_2{=}CHCH_2CH_3$ (1-butene), which has the double bond between the first and second carbon atoms in the chain. The other two structures have the double bond between the second and third carbon atoms and are forms of $CH_3CH{=}CHCH_3$ (2-butene). All four carbon atoms in 2-butene lie in the same plane, so there are two possible structures (part (a) in Figure 3.7.2). If the two methyl groups are on the same side of the double bond, the compound is *cis*-2-butene (from the Latin *cis*, meaning “on the same side”). If the two methyl groups are on opposite sides of the double bond, the compound is *trans*-2-butene (from the Latin *trans*, meaning “across”). These are distinctly different molecules: *cis*-2-butene melts at –138.9°C, whereas *trans*-2-butene melts at –105.5°C.

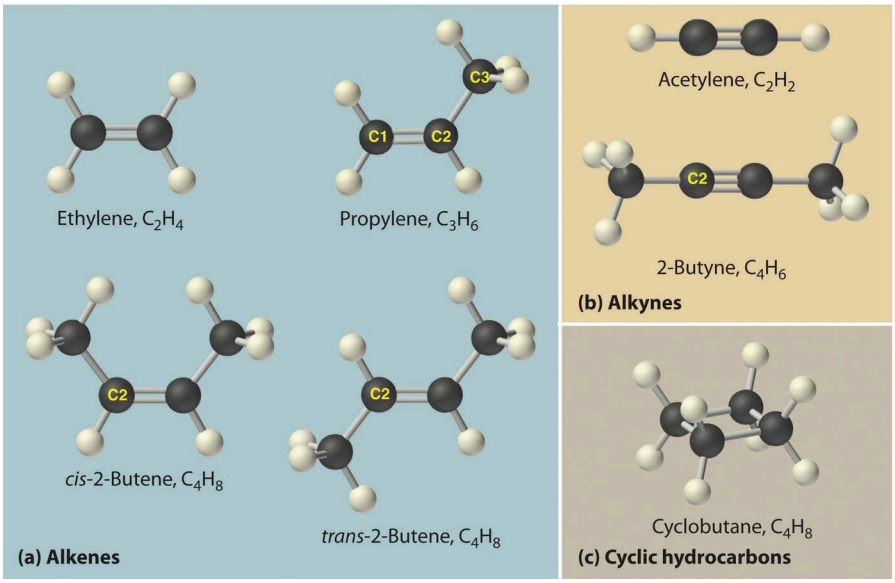
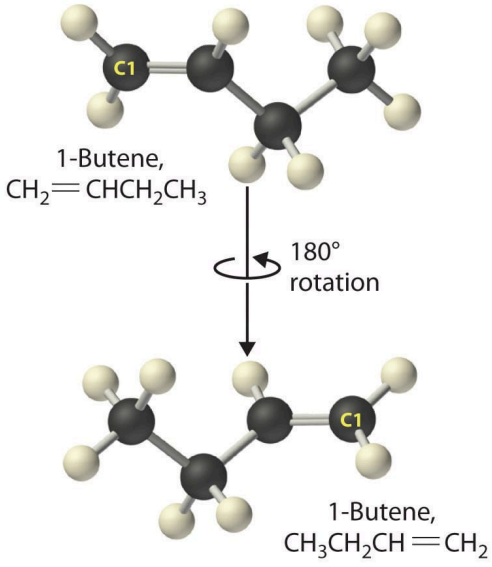


Figure 3.7.2: Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons. The positions of the carbon atoms in the chain are indicated by C_1 or C_2.

Just as a number indicates the positions of branches in an alkane, the number in the name of an alkene specifies the position of the *first* carbon atom of the double bond. The name is based on the lowest possible number starting from *either end* of the carbon chain, so $CH_3CH_2CH{=}CH_2$ is called 1-butene, *not* 3-butene. Note that $CH_2{=}CHCH_2CH_3$ and $CH_3CH_2CH{=}CH_2$ are different ways of writing the *same molecule* (1-butene) in two different orientations.



The name of a compound does *not* depend on its orientation. *As illustrated for 1-butene, both condensed structural formulas and molecular models show different orientations of the same molecule. It is important to be able to recognize the same structure no matter what its orientation.*

Note

The positions of groups or multiple bonds are always indicated by the lowest number possible.

Alkynes

The simplest alkyne is *acetylene*, C_2H_2 or HC≡CH (part (b) in Figure 3.7.2). Because a mixture of acetylene and oxygen burns with a flame that is hot enough (>3000°C) to cut metals such as hardened steel, acetylene is widely used in cutting and welding torches. The names of other alkynes are similar to those of the corresponding alkanes but end in *-yne*. For example, $HC{\equiv}CCH_3$ is *propyne*, and $CH_3C{\equiv}CCH_3$ is *2-butyne* because the multiple bond begins on the second carbon atom.

> **Note**
>
> The number of bonds between carbon atoms in a hydrocarbon is indicated in the suffix:
>
> - alk*ane*: only carbon–carbon single bonds
> - alk*ene*: at least one carbon–carbon double bond
> - alk*yne*: at least one carbon–carbon triple bond

Cyclic Hydrocarbons

In a cyclic hydrocarbon, the ends of a hydrocarbon chain are connected to form a ring of covalently bonded carbon atoms. Cyclic hydrocarbons are named by attaching the prefix *cyclo-* to the name of the alkane, the alkene, or the alkyne. The simplest cyclic alkanes are *cyclopropane* (C_3H_6) a flammable gas that is also a powerful anesthetic, and *cyclobutane* (C_4H_8) (part (c) in Figure 3.7.2). The most common way to draw the structures of cyclic alkanes is to sketch a polygon with the same number of vertices as there are carbon atoms in the ring; each vertex represents a CH_2 unit. The structures of the cycloalkanes that contain three to six carbon atoms are shown schematically in Figure 3.7.3.

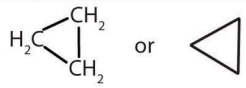
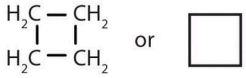
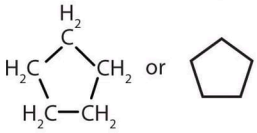
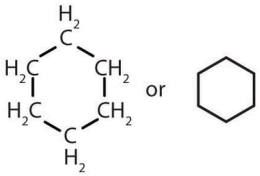
Name	Molecular Formula	Structural Formula
cyclopropane	C_3H_6	
cyclobutane	C_4H_8	
cyclopentane	C_5H_{10}	
cyclohexane	C_6H_{12}	

Figure 3.7.3: The Simple Cycloalkanes

Aromatic Hydrocarbons

Alkanes, alkenes, alkynes, and cyclic hydrocarbons are generally called aliphatic hydrocarbons. The name comes from the Greek *aleiphar*, meaning “oil,” because the first examples were extracted from animal fats. In contrast, the first examples of **aromatic hydrocarbons**, also called *arenes*, were obtained by the distillation and degradation of highly scented (thus *aromatic*) resins from tropical trees.

The simplest aromatic hydrocarbon is *benzene* (C_6H_6), which was first obtained from a coal distillate. The word *aromatic* now refers to benzene and structurally similar compounds. As shown in part (a) in Figure 3.7.4, it is possible to draw the structure of benzene in two different but equivalent ways, depending on which carbon atoms are connected by double bonds or single bonds.

Toluene is similar to benzene, except that one hydrogen atom is replaced by a $-CH_3$ group; it has the formula C_7H_8 (part (b) in Figure 3.7.4). The chemical behavior of aromatic compounds differs from the behavior of aliphatic compounds. Benzene and toluene are found in gasoline, and benzene is the starting material for preparing substances as diverse as aspirin and nylon.

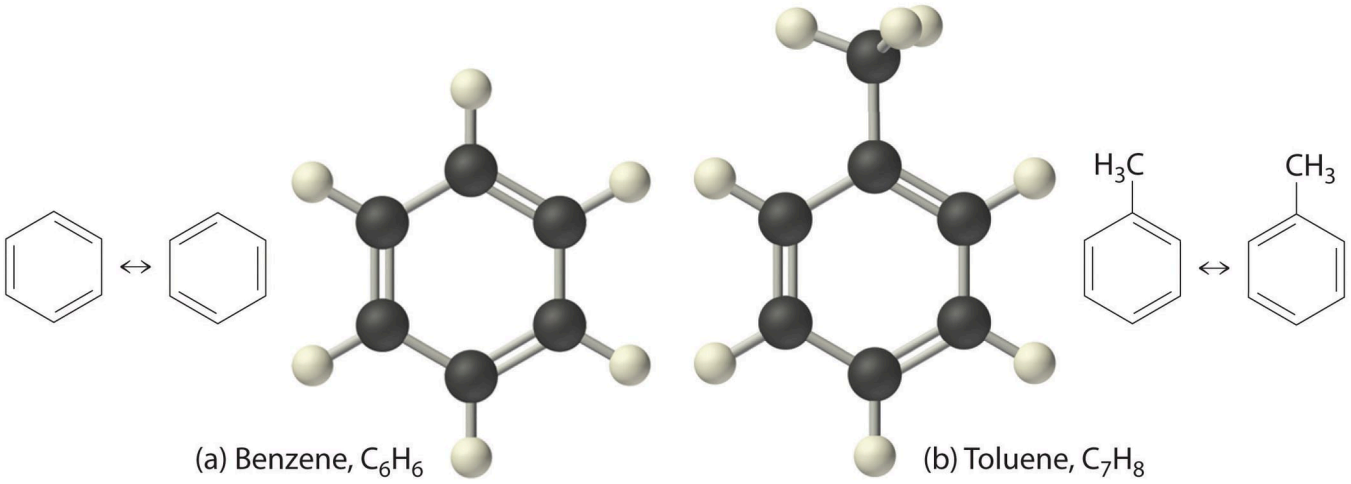


Figure 3.7.4: *Two Aromatic Hydrocarbons: (a) Benzene and (b) Toluene*

Figure 3.7.5 illustrates two of the molecular structures possible for hydrocarbons that have six carbon atoms. As shown, compounds with the same molecular formula can have very different structures.

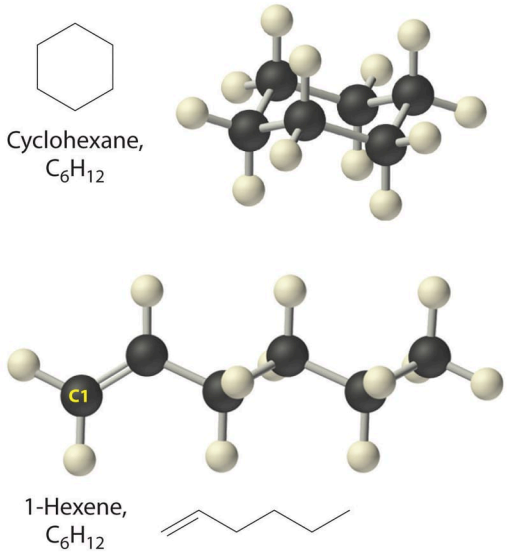


Figure 3.7.5: Two Hydrocarbons with the Molecular Formula C_6H_{12}

Example 3.7.1

Write the condensed structural formula for each hydrocarbon.

a. n-heptane
b. 2-pentene
c. 2-butyne
d. cyclooctene

Given: name of hydrocarbon

Asked for: condensed structural formula

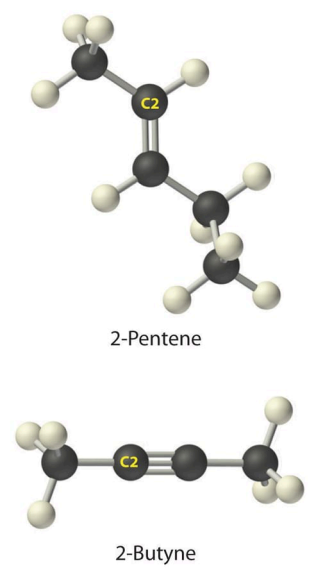
Strategy:

A. Use the prefix to determine the number of carbon atoms in the molecule and whether it is cyclic. From the suffix, determine whether multiple bonds are present.
B. Identify the position of any multiple bonds from the number(s) in the name and then write the condensed structural formula.

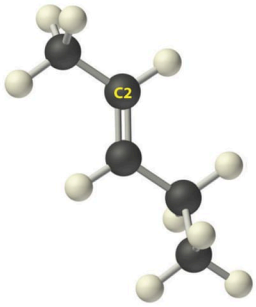
Solution:

a. **A** The prefix hept- tells us that this hydrocarbon has seven carbon atoms, and n- indicates that the carbon atoms form a straight chain. The suffix -ane tells that it is an alkane, with no carbon–carbon double or triple bonds. **B** The condensed structural formula is $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$, which can also be written as $CH_3(CH_2)_5CH_3$.

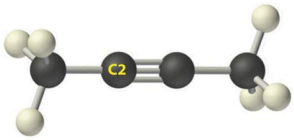
b. **A** The prefix pent- tells us that this hydrocarbon has five carbon atoms, and the suffix -ene indicates that it is an alkene, with a carbon–carbon double bond. **B** The 2- tells us that the double bond begins on the second carbon of the five-carbon atom chain. The condensed structural formula of the compound is therefore $CH_3CH{=}CHCH_2CH_3$.



c. **A** The prefix but- tells us that the compound has a chain of four carbon atoms, and the suffix -yne indicates that it has a carbon–carbon triple bond. **B** The 2- tells us that the triple bond begins on the second carbon of the four-carbon atom chain. So the condensed structural formula for the compound is $CH_3C{\equiv}CCH_3$.

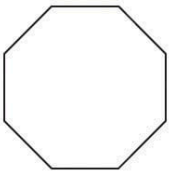


2-Pentene

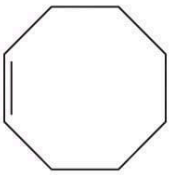


2-Butyne

d. A The prefix cyclo- tells us that this hydrocarbon has a ring structure, and oct- indicates that it contains eight carbon atoms, which we can draw as



The suffix -ene tells us that the compound contains a carbon–carbon double bond, but where in the ring do we place the double bond? B Because all eight carbon atoms are identical, it doesn't matter. We can draw the structure of cyclooctene as



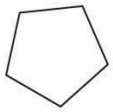
Exercise 3.7.1

Write the condensed structural formula for each hydrocarbon.

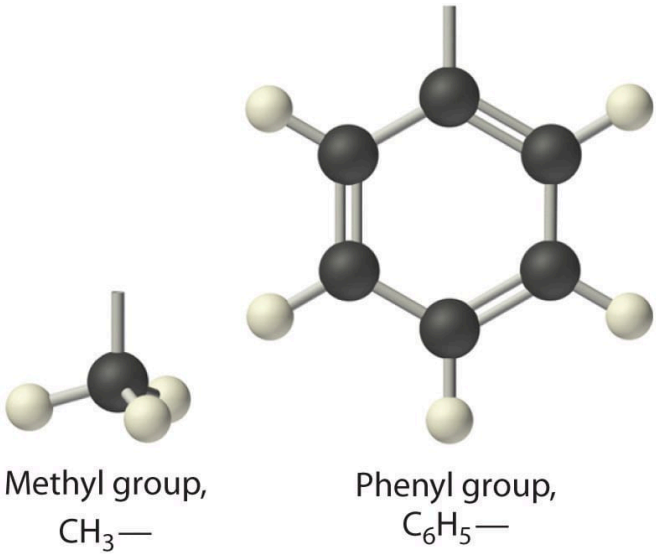
a. n-octane
b. 2-hexene
c. 1-heptyne
d. cyclopentane

Answer:

a. $CH_3(CH_2)_6CH_3$
b. $CH_3CH{=}CHCH_2CH_2CH_3$
c. $HC{\equiv}C(CH_2)_4CH_3$

d. 

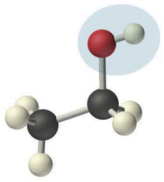
The general name for a group of atoms derived from an alkane is an *alkyl group*. The name of an alkyl group is derived from the name of the alkane by adding the suffix *-yl*. Thus the $-CH_3$ fragment is a *methyl* group, the $-CH_2CH_3$ fragment is an *ethyl* group, and so forth, where the dash represents a single bond to some other atom or group. Similarly, groups of atoms derived from aromatic hydrocarbons are *aryl groups*, which sometimes have unexpected names. For example, the $-C_6H_5$ fragment is derived from benzene, but it is called a *phenyl* group. In general formulas and structures, alkyl and aryl groups are often abbreviated as R.



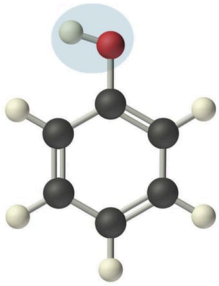
Structures of alkyl and aryl groups. *The methyl group is an example of an alkyl group, and the phenyl group is an example of an aryl group.*

Alcohols

Replacing one or more hydrogen atoms of a hydrocarbon with an –OH group gives an alcohol, represented as ROH. The simplest alcohol (CH_3OH) is called either *methanol* (its systematic name) or *methyl alcohol* (its common name). Methanol is the antifreeze in automobile windshield washer fluids, and it is also used as an efficient fuel for racing cars, most notably in the Indianapolis 500. Ethanol (or ethyl alcohol, CH_3CH_2OH) is familiar as the alcohol in fermented or distilled beverages, such as beer, wine, and whiskey; it is also used as a gasoline additive (Section 2.6). The simplest alcohol derived from an aromatic hydrocarbon is C_6H_5OH, *phenol* (shortened from *phenyl* alcohol), a potent disinfectant used in some sore throat medications and mouthwashes.



Ethanol, CH_3CH_2OH



Phenol, C_6H_5OH

Ethanol, which is easy to obtain from fermentation processes, has successfully been used as an alternative fuel for several decades. Although it is a “green” fuel when derived from plants, it is an imperfect substitute for fossil fuels because it is less efficient than gasoline. Moreover, because ethanol absorbs water from the atmosphere, it can corrode an engine’s seals. Thus other types of processes are being developed that use bacteria to create more complex alcohols, such as octanol, that are more energy efficient and that have a lower tendency to absorb water. As scientists attempt to reduce mankind’s dependence on fossil fuels, the development of these so-called *biofuels* is a particularly active area of research.

Summary

The simplest organic compounds are the **hydrocarbons**, which contain *only* carbon and hydrogen. **Alkanes** contain only carbon–hydrogen and carbon–carbon single bonds, **alkenes** contain at least one carbon–carbon double bond, and **alkynes** contain one or more carbon–carbon triple bonds. Hydrocarbons can also be **cyclic**, with the ends of the chain connected to form a ring. Collectively, alkanes, alkenes, and alkynes are called **aliphatic hydrocarbons**. **Aromatic hydrocarbons**, or *arenes*, are another important class of hydrocarbons that contain rings of carbon atoms related to the structure of benzene (C_6H_6). A derivative of an alkane or an arene from which one hydrogen atom has been removed is called an *alkyl group* or an *aryl group*, respectively. **Alcohols** are another common class of organic compound, which contain an –OH group covalently bonded to either an alkyl group or an aryl group (often abbreviated **R**).

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3.E: Homework Problems

3.1: Types of Chemical Compounds and their Formulas

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. the forces that hold the atoms together.

    b. melting points.

    c. physical states at room temperature and pressure.

7. Why do covalent compounds generally tend to have lower melting points than ionic compounds?

Answer 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. 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. 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. ${}^{27}_{13}X^{3+}$

Answers

5.

a. 27

b. 38

c. 54

d. 28

e. 67

f. 18

9.

a. Li, Li^{+}, 2nd period, group 1

b. F, F^{-}, 2nd period, group 17

c. Al, Al^{3+}, 3nd period, group 13

Conceptual Problems2

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

2. Classify each compound as ionic or covalent.

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

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

1. $CH_3CH_2CO_2H$
2. $CaCl_2$
3. $Y(NO_3)_3$
4. H_2S
5. $NaC_2H_3O_2$

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?

Answers 2

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 $(CH_3)_2S$.

Numerical Problems 2

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

Answers

1.

a. $MgSO_4$

b. $C_2H_6O_2$

c. $C_2H_4O_2$

d. $KClO_3$

e. $NaOCl{\cdot}5H_2O$

3.

Ion	K +	Fe 3+	NH 4 +	Ba 2+
Cl –	KCl	FeCl3	NH4Cl	BaCl2
SO 4 2–	K2SO4	Fe2(SO4)3	(NH4)2SO4	BaSO4
PO 4 3–	K3PO4	FePO4	(NH4)3PO4	Ba3(PO4)2
NO 3 –	KNO3	Fe(NO3)3	NH4NO3	Ba(NO3)2
OH –	KOH	Fe(OH)3	NH4OH	Ba(OH)2

5.

a. Li_3N

b. CsCl

c. GeO_2

d. Rb_2S

e. Na_3As

7.

a. $AlCl_3$

b. $K_2Cr_2O_7$

c. CH_2

d. CH_5N_3

e. CH_2O

3.6: Names and Formulas of Inorganic Compounds

Conceptual Problems

1. Name each cation.

1. a. K+
2. b. Al3+
3. c. NH4+
4. d. Mg2+
5. e. Li+

2. Name each anion.

1. a. Br^-
2. b. CO_3^{2-}
3. c. S^{2-}
4. d. NO_3^-
5. e. HCO_2^-
6. f. F^-
7. g. ClO^-
8. h. $C_2O_4^{2-}$

3. Name each anion.

1. a. PO_4^{3-}
2. b. Cl^-
3. c. SO_3^{2-}
4. d. $CH_3CO_2^-$
5. e. HSO_4^-
6. f. ClO_4^-
7. g. NO_2^-
8. h. O^{2-}

4. Name each anion.

1. a. SO_4^{2-}
2. b. CN^-
3. c. $Cr_2O_7^{2-}$
4. d. N^{3-}
5. e. OH^-
6. f. I^-
7. g. O_2^{2-}

5. Name each compound.

1. a. $MgBr_2$
2. b. NH_4CN
3. c. CaO
4. d. $KClO_3$
5. e. K_3PO_4

6. f. NH_4NO_2
7. g. NaN_3

6. Name each compound.

1. a. $NaNO_3$
2. b. $Cu_3(PO_4)_2$
3. c. NaOH
4. d. Li_4C
5. e. CaF_2
6. f. NH_4Br
7. g. $MgCO_3$

7. Name each compound.

1. a. RbBr
2. b. $Mn_2(SO_4)_3$
3. c. NaClO
4. d. $(NH4)_2SO_4$
5. e. NaBr
6. f. KIO_3
7. g. Na_2CrO_4

8. Name each compound.

1. a. NH_4ClO_4
2. b. $SnCl_4$
3. c. $Fe(OH)_2$
4. d. Na_2O
5. e. $MgCl_2$
6. f. K_2SO_4
7. g. $RaCl_2$

9. Name each compound.

1. a. KCN
2. b. LiOH
3. c. $CaCl_2$
4. d. $NiSO_4$
5. e. NH_4ClO_2
6. f. $LiClO_4$
7. g. $La(CN)_3$

Answer

7.

a. rubidium bromide

b. manganese(III) sulfate

c. sodium hypochlorite

d. ammonium sulfate

e. sodium bromide

f. potassium iodate

g. sodium chromate

Numerical Problems

1. For each ionic compound, name the cation and the anion and give the charge on each ion.

1. a. BeO
2. b. $Pb(OH)_2$
3. c. BaS
4. d. $Na_2Cr_2O_7$
5. e. $ZnSO_4$
6. f. KClO
7. g. NaH_2PO_4

2. For each ionic compound, name the cation and the anion and give the charge on each ion.

1. a. $Zn(NO_3)_2$
2. b. CoS
3. c. $BeCO_3$
4. d. Na_2SO_4
5. e. $K_2C_2O_4$
6. f. NaCN
7. g. $FeCl_2$

3. Write the formula for each compound.

1. a. magnesium carbonate
2. b. aluminum sulfate
3. c. potassium phosphate
4. d. lead(IV) oxide
5. e. silicon nitride
6. f. sodium hypochlorite
7. g. titanium(IV) chloride
8. h. disodium ammonium phosphate

4. Write the formula for each compound.

1. a. lead(II) nitrate
2. b. ammonium phosphate
3. c. silver sulfide
4. d. barium sulfate
5. e. cesium iodide
6. f. sodium bicarbonate
7. g. potassium dichromate
8. h. sodium hypochlorite

5. Write the formula for each compound.

1. a. zinc cyanide
2. b. silver chromate
3. c. lead(II) iodide
4. d. benzene
5. e. copper(II) perchlorate

6. Write the formula for each compound.

1. a. calcium fluoride
2. b. sodium nitrate
3. c. iron(III) oxide
4. d. copper(II) acetate
5. e. sodium nitrite

7. Write the formula for each compound.

1. a. sodium hydroxide
2. d. calcium cyanide
3. c. magnesium phosphate
4. d. sodium sulfate
5. e. nickel(II) bromide
6. f. calcium chlorite
7. g. titanium(IV) bromide

8. Write the formula for each compound.

1. a. sodium chlorite
2. b. potassium nitrite
3. c. sodium nitride (also called sodium azide)
4. d. calcium phosphide
5. e. tin(II) chloride
6. f. calcium hydrogen phosphate
7. g. iron(II) chloride dihydrate

9. Write the formula for each compound.

1. a. potassium carbonate
2. b. chromium(III) sulfite
3. c. cobalt(II) phosphate
4. d. magnesium hypochlorite
5. e. nickel(II) nitrate hexahydrate

Conceptual Problems

1. Name each acid.

1. a. HCl
2. b. $HBrO_3$
3. c. HNO_3
4. d. H_2SO_4
5. e. HIO_3

2. Name each acid.

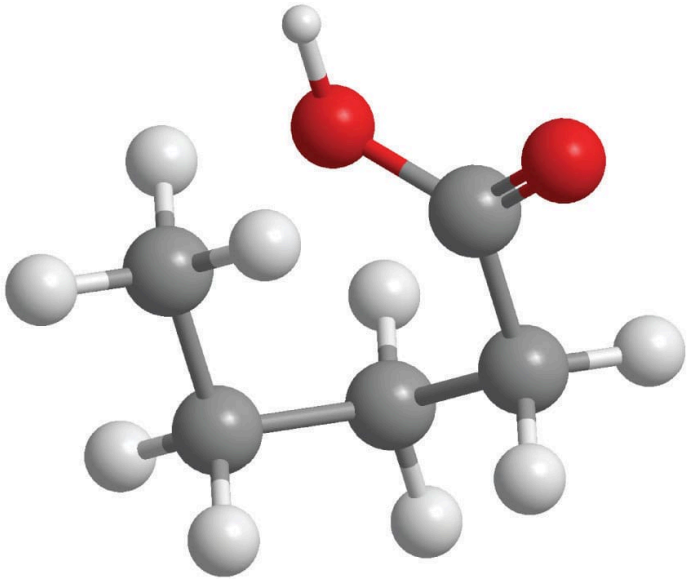
1. a. HBr
2. b. H_2SO_3
3. c. $HClO_3$
4. d. HCN
5. e. H_3PO_4

3. Name the aqueous acid that corresponds to each gaseous species.

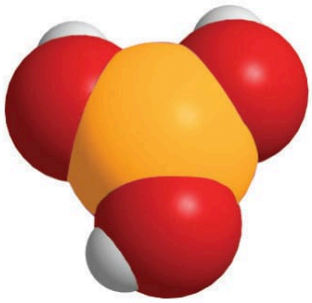
1. a. hydrogen bromide
2. b. hydrogen cyanide
3. c. hydrogen iodide

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

a.

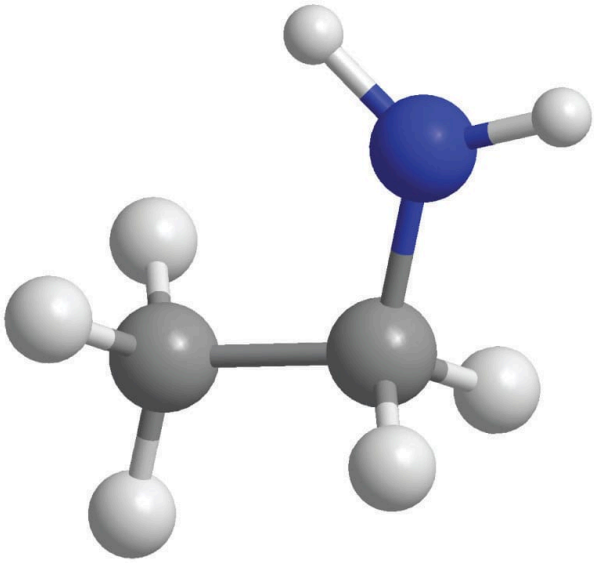


b.

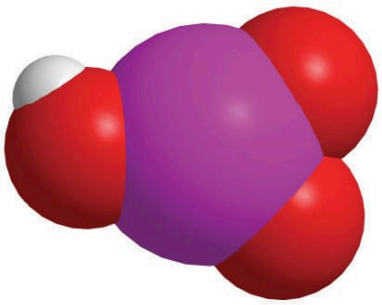


5. For each structural formula, write the condensed formula and the name of the compound.

a.



b.



6. When each compound is added to water, is the resulting solution acidic, neutral, or basic?

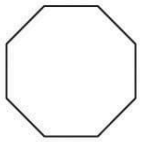
1. a. CH_3CH_2OH
2. b. $Mg(OH)_2$
3. c. $C_6H_5CO_2H$
4. d. LiOH
5. e. $C_3H_7CO_2H$
6. f. H_2SO_4

7. Draw the structure of the simplest example of each type of compound.

1. a. alkane
2. b. alkene
3. c. alkyne
4. d. aromatic hydrocarbon
5. e. alcohol
6. f. carboxylic acid
7. g. amine
8. h. cycloalkane

8. Identify the class of organic compound represented by each compound.

a.



b. CH_3CH_2OH

c. $HC{\equiv}CH$

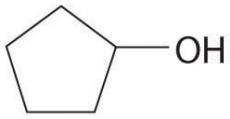
d.



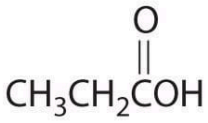
e. $C_3H_7NH_2$

f. $CH_3CH{=}CHCH_2CH_3$

g.



h.



9. Identify the class of organic compound represented by each compound.

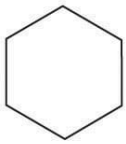
a.



b.



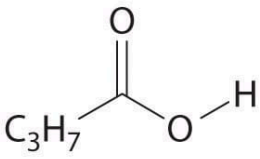
c.



d.

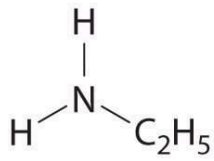


e.

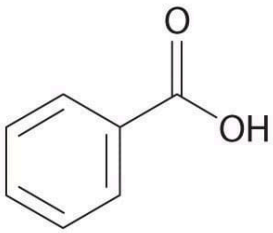


f. $CH_3C{\equiv}CH$

g.



h.



Numerical Problems

1. Write the formula for each compound.

1. a. hypochlorous acid
2. b. perbromic acid
3. c. hydrobromic acid
4. d. sulfurous acid
5. e. sodium perbromate

2. Write the formula for each compound.

1. a. hydroiodic acid
2. b. hydrogen sulfide
3. c phosphorous acid
4. d. perchloric acid
5. e. calcium hypobromite

3. Name each compound.

1. a. HBr
2. b. H_2SO_3
3. c. HCN
4. d. $HClO_4$
5. e. $NaHSO_4$

4. Name each compound.

1. a. H_2SO_4
2. b. HNO_2
3. c. K_2HPO_4
4. d. H_3PO_3
5. e. $Ca(H_2PO_4)_2 \cdot H_2O$

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4: CHEMICAL REACTIONS

Petrucci: *General Chemistry*
Principles and Modern Applications

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4.1: Chemical Reactions and Chemical Equations

$$2H_2 + O_2 \rightarrow 2H_2O \tag{4.1.1}$$

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 4.1.1 is

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O \tag{4.1.2}$$

$$reactant \qquad products \tag{4.1.3}$$

The arrow is read as “yields” or “reacts to form.” Equation 4.1.1 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:

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_{3\ (s)} + N_{2\ (g)} + 4H_2O_{(g)} \tag{4.1.4}$$

Equation 4.1.2 is identical to Equation 4.1.1 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 4.1.1 and 4.1.2. 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 4.1.1 and 4.1.2 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.

of two substances in a chemical reaction is the ratio of their coefficients in the balanced chemical equation.

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Introduction to Chemical Reaction Equations: https://youtu.be/5mjawuf7K2Q

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4.2: Chemical Equations and Stoichiometry

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \tag{4.2.1}$$

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 in , 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:

$$moles\,glucose = 45.3\,g\,glucose \times \frac{1\,mol\,glucose}{180.2\,g\,glucose} = 0.251\,mol\,glucose \tag{4.2.2}$$

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

$$moles\,CO_2 = mol\,glucose \times \frac{6\,mol\,CO_2}{1\,mol\,glucose} \tag{4.2.3}$$

$$= 0.251\,mol\,glucose \times \frac{6\,mol\,CO_2}{1\,mol\,glucose} \tag{4.2.4}$$

$$= 1.51\,mol\,CO_2 \tag{4.2.5}$$

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:

$$mass\,of\,CO_2 = 1.51\,mol\,CO_2 \times \frac{44.010\,g\,CO_2}{1\,mol\,CO_2} = 66.5\,g\,CO_2 \tag{4.2.6}$$

$$45.3\,g\,glucose \times \frac{1\,mol\,glucose}{180.2\,g\,glucose} \times \frac{6\,mol\,CO_2}{1\,mol\,glucose} \times \frac{44.010\,g\,CO_2}{1\,mol\,CO_2} = 66.4\,g\,CO_2 \tag{4.2.7}$$

Discrepancies between the two values are attributed to rounding errors resulting from using stepwise calculations in steps 1–3. (For more information about rounding and significant digits, see Essential Skills 1 in , .) 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 11, the mass of one reactant that is required to consume a given mass of another reactant.

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.

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Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors (Mol Ratios): https://youtu.be/74mHV0CZcjw

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4.3: Chemical Reactions in Solution

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 a common unit of concentration and 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:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution}$$

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,

$$[\text{sucrose}] = 1.00\ \text{M} \tag{4.3.1}$$

is read as “the concentration of sucrose is 1.00 molar.” The relationships between volume, molarity, and moles may be expressed as either

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{4.3.2}$$

or

$$V_{mL} M_{mmol/mL} = \cancel{mL}\left(\frac{mmol}{\cancel{mL}}\right) = mmoles \tag{4.3.3}$$

Figure 4.3.1 illustrates the use of Equation 4.3.2 and Equation 4.3.3.



(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 4.3.1: Preparation of a Solution of Known Concentration Using a Solid Solute

Example 4.3.1

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 4.3.2 or Equation 4.3.3, 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 4.3.2 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 4.3.1

Calculate the number of millimoles of alanine, a biologically important molecule, in 27.2 mL of 1.53 M alanine.

Answer: 41.6 mmol

Concentrations are 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 (Table 4.3.1).

Table 4.3.1: 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

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Calculations Involving Molarity (M): https://youtu.be/TVTCvKoSR-Q

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 4.3.1 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 4.3.2, for some substances this effect can be significant, especially for concentrated solutions.

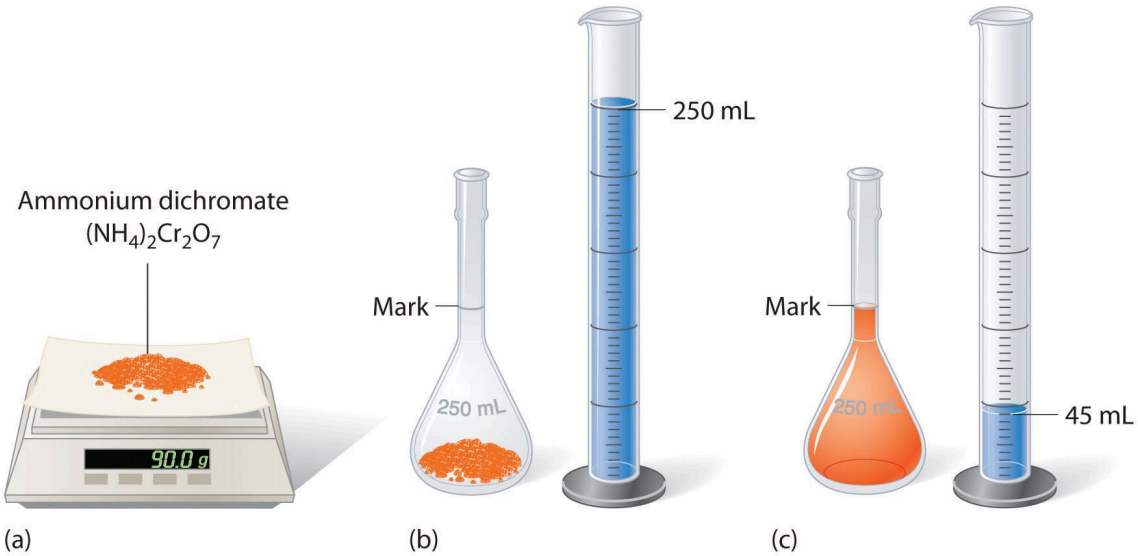


Figure 4.3.2: Preparation of 250 mL of a Solution of $(NH_4)_2Cr_2O_7$ in Water. The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.

Example 4.3.2

The solution in Figure 4.3.1 contains 10.0 g of cobalt(II) chloride dihydrate, $CoCl_2 \bullet 2H_2O$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $CoCl_2 \bullet 2H_2O$?

Given: mass of solute and volume of solution

Asked for: concentration (M)

Strategy:

To find the number of moles of $CoCl_2 \bullet 2H_2O$, 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 $CoCl_2 \bullet 2H_2O$ 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 4.3.2

The solution shown in Figure 4.3.2 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: $(NH_4)_2Cr_2O_7 = 1.43\ \ M$

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 4.3.2. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example 4.3.3.

Example 4.3.3

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 4.3.3

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: 2.3 g NaCl

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 a commercially prepared solution of known concentration, 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 4.3.3. 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

$$(V_s)(M_s) = moles \ \ of \ \ solute = (V_d)(M_d)$$

where the subscripts s and *d* indicate the stock and dilute solutions, respectively. Example 5.5.4 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 4.3.3: 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 4.3.4

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example 4.3.3?

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 4.3.3 was 0.310 M glucose. We begin by using Equation 4.3.4 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 4.3.4 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 4.3.4

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: 16 mL

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.

The flowchart for stoichiometric calculations illustrated in Figure 4.3.4 shows that in 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.

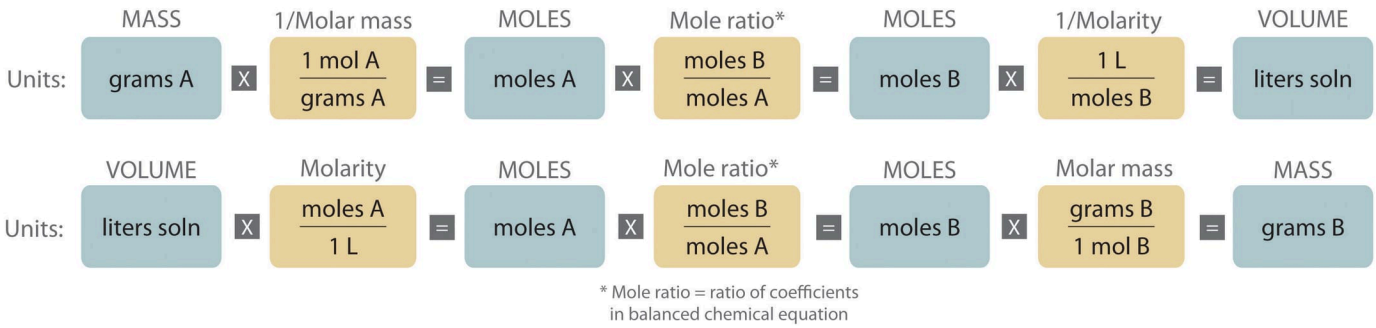


Figure 4.3.4: An Expanded Flowchart for Stoichiometric Calculations. Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in a balanced chemical equation.

Note

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 4.3.5: 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:

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s) \tag{4.3.4}$$

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

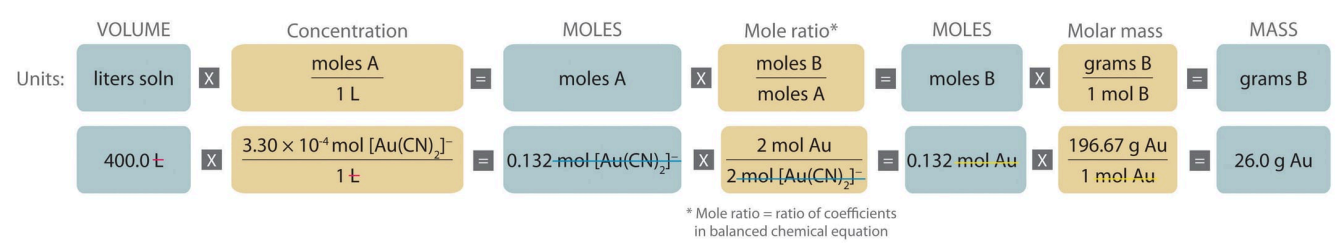
Asked for: mass of product

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 4.3.2 is adapted for this particular problem as follows:



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:

$$moles\ [Au(CN)_2]^- = V_L M_{mol/L} \tag{4.3.5}$$

$$= 400.0\ \cancel{L}\left(\frac{3.30 \times 10^{4-}\ mol\ [Au(CN)_2]^-}{1\ \cancel{L}}\right) = 0.132\ mol\ [Au(CN)_2]^- \tag{4.3.6}$$

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:

$$mass\ of\ Au = (moles\ Au)(molar\ mass\ Au) \tag{4.3.7}$$

$$= 0.132\ \cancel{mol\ Au}\left(\frac{196.97\ g\ Au}{1\ \cancel{mol\ Au}}\right) = 26.0\ g\ Au \tag{4.3.8}$$

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 4.3.5: 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: 3.89 g

Ion Concentrations in Solution

In Example 4.3.2, 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:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{H_2O(l)} 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \tag{4.3.9}$$

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 4.3.4).

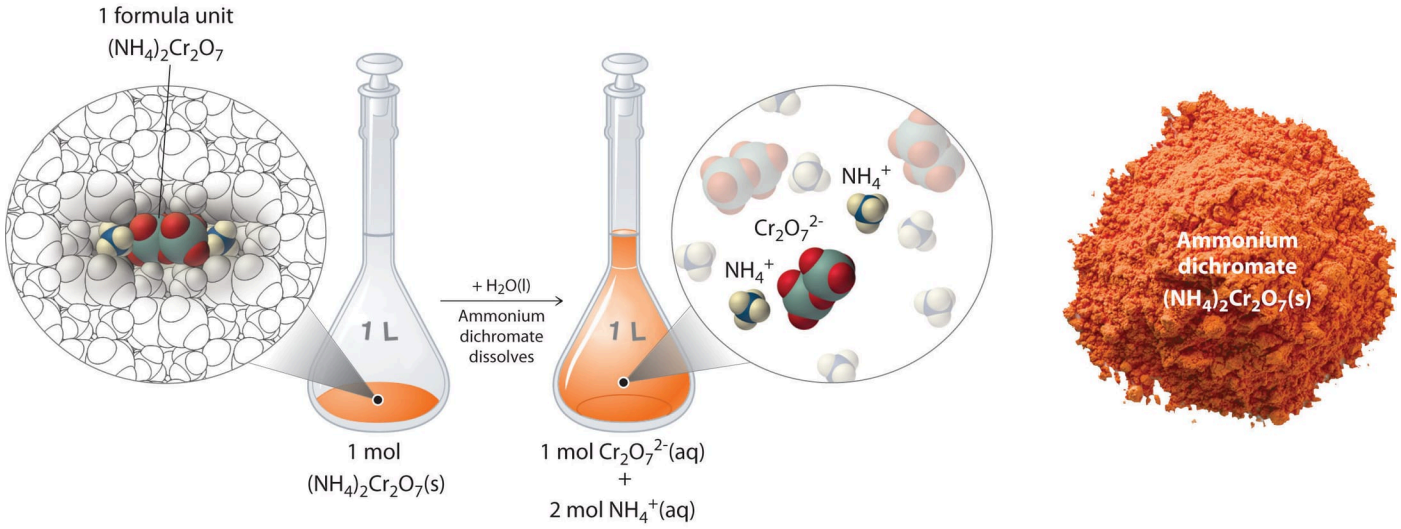


Figure 4.3.4: Dissolution of 1 mol of an Ionic Compound. In this case, dissolving 1 mol of $(NH_4)_2Cr_2O_7$ produces a solution that contains 1 mol of $Cr_2O_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)

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.

Example 4.3.6

What are the concentrations of all species derived from the solutes in these aqueous solutions?

1. 0.21 M NaOH
2. 3.7 M $(CH_3)CHOH$
3. 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:

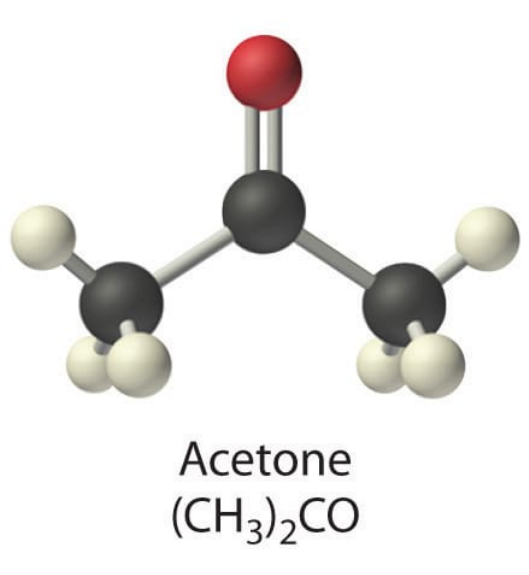
   $$In(NO_3)_3(s) \xrightarrow{H_2O(l)} In^{3+}(aq) + 3NO_3^-(aq)$$

   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 4.3.6

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



Answer

a. $[Ba^{2+}] = 0.0012\ M;\ [OH^-] = 0.0024\ M$
b. $[Na^+] = 0.34\ M;\ [SO_4^{2-}] = 0.17\ M$
c. $[(CH_3)_2CO] = 0.50\ M$

YouTube Video

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View this YouTube Video online

Concentration of Ions in Solution from a Soluble Salt: https://youtu.be/qsekSJBLemc

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:**

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{4.3.10}$$

- **relationship among volume, molarity, and moles**:

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{4.3.11}$$

- **relationship between volume and concentration of stock and dilute solutions**:

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d) \tag{4.3.12}$$

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.

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4.4: Determining the Limiting Reactant

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

$$1\,\text{box mix} + 2\,\text{eggs} \rightarrow 1\,\text{batch brownies} \tag{4.4.1}$$

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.

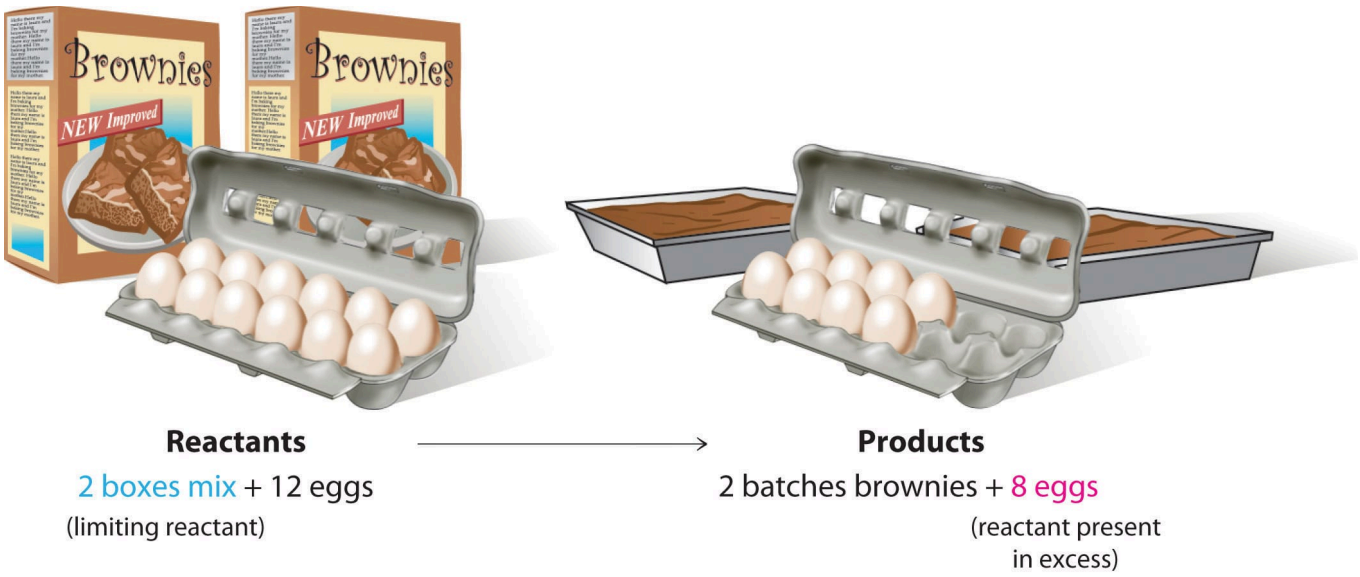


Figure 4.4.1: The Concept of a Limiting Reactant in the Preparation of Brownies

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 ($TiCl_4$) and carbon dioxide. Titanium tetrachloride is then converted to metallic titanium by reaction with magnesium metal at high temperature:

$$TiCl_4(g) + 2\,Mg(l) \rightarrow Ti(s) + 2\,MgCl_2(l) \tag{4.4.2}$$

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 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 the equation above? 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.

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:

$$moles\,TiCl_4 = \frac{mass\,TiCl_4}{molar\,mass\,TiCl_4} \tag{4.4.3}$$

$$= 1000\,g\,TiCl_4 \times \frac{1\,mol\,TiCl_4}{189.679\,g\,TiCl_4} = 5.272\,mol\,TiCl_4 \tag{4.4.4}$$

$$moles\,Mg = \frac{mass\,Mg}{molar\,mass\,Mg} \tag{4.4.5}$$

$$= 200\,g\,Mg \times \frac{1\,mol\,Mg}{24.305\,g\,Mg} = 8.23\,mol\,Mg \tag{4.4.6}$$

2. There are more moles of magnesium than of titanium tetrachloride, but the ratio is only the following:

$$\frac{mol\,Mg}{mol\,TiCl_4} = \frac{8.23\,mol}{5.272\,mol} = 1.56 \tag{4.4.7}$$

Because the ratio of the coefficients in the balanced chemical equation is,

$$\frac{2\,mol\,Mg}{1\,mol\,TiCl_4} = 2 \tag{4.4.8}$$

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 $TiCl_4$ are required for complete reaction. Because there are 5.272 mol of $TiCl_4$, titanium tetrachloride is present in excess. Conversely, 5.272 mol of $TiCl_4$ requires 2 × 5.272 = 10.54 mol of Mg, but there are only 8.23 mol. Therefore, magnesium is the limiting reactant.

3. Because magnesium is the limiting reactant, the number of moles of magnesium determines the number of moles of titanium that can be formed:

$$moles\,Ti = 8.23\,mol\,Mg = \frac{1\,mol\,Ti}{2\,mol\,Mg} = 4.12\,mol\,Ti \tag{4.4.9}$$

Thus only 4.12 mol of Ti can be formed.

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):

$$moles\,Ti = mass\,Ti \times molar\,mass\,Ti = 4.12\,mol\,Ti \times \frac{47.867\,g\,Ti}{1\,mol\,Ti} = 197\,g\,Ti \tag{4.4.10}$$

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 $TiCl_4$ 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:

$$TiCl_4 : \frac{5.272\,mol\,(actual)}{1\,mol\,(stoich)} = 5.272 \quad Mg : \frac{8.23\,mol\,(actual)}{2\,mol\,(stoich)} = 4.12 \tag{4.4.11}$$

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 4.4.1 demonstrates.

YouTube Video

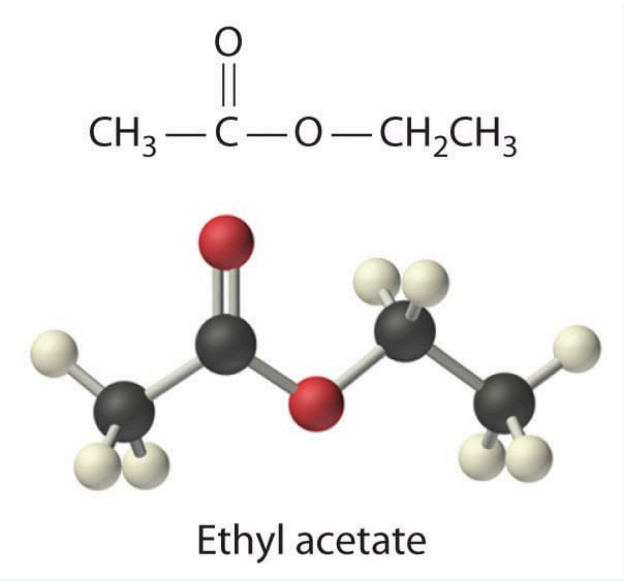
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Determining the Limiting Reactant and Theoretical Yield for a Reaction: https://youtu.be/HmDm1qpNUD0

Example 4.4.1: 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:

$$C_2H_5OH(l) + CH_3CO_2H(aq) \rightarrow CH_3CO_2C_2H_5(aq) + H_2O(l) \tag{4.4.12}$$

B We need to calculate the number of moles of ethanol and acetic acid that are present in 10.0 mL of each. Recall from that the density of a substance is the mass divided by the volume:

$$density = \frac{mass}{volume} \tag{4.4.13}$$

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):

$$moles\, C_2H_5OH = \frac{mass\, C_2H_5OH}{molar\, mass\, C_2H_5OH} \tag{4.4.14}$$

$$= \frac{volume\, C_2H_5OH \times density\, C_2H_5OH}{molar\, mass\, C_2H_5OH} \tag{4.4.15}$$

$$= 10.0\, ml\, C_2H_5OH \times \frac{0.7893\, g\, C_2H_5OH}{1\, ml\, C_2H_5OH} \times \frac{1\, mole\, C_2H_5OH}{46.07\, g\, C_2H_5OH} \tag{4.4.16}$$

$$= 0.171\, mol\, C_2H_5OH \tag{4.4.17}$$

$$moles\, CH_3CO_2H = \frac{mass\, CH_3CO_2H}{molar\, mass\, CH_3CO_2H} \tag{4.4.18}$$

$$= \frac{volume\, CH_3CO_2H \times density\, CH_3CO_2H}{molar\, mass\, CH_3CO_2H} \tag{4.4.19}$$

$$= 10.0\, ml\, CH_3CO_2H \times \frac{1.0492\, g\, CH_3CO_2H}{1\, ml\, CH_3CO_2H} \times \frac{1\, mol\, CH_3CO_2H}{60.05\, g\, CH_3CO_2H} \tag{4.4.20}$$

$$= 0.175\, mol\, CH_3CO_2H \tag{4.4.21}$$

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:

$$moles\, ethyl\, acetate = molethanol \times \frac{1\, mol\, ethyl\, acetate}{1\, mol\, ethanol} \tag{4.4.22}$$

$$= 0.171\, mol\, C_2H_5OH \times \frac{1\, mol\, CH_3CO_2C_2H_5}{1\, mol\, C_2H_5OH} \tag{4.4.23}$$

$$= 0.171\, mol\, CH_3CO_2C_2H_5 \tag{4.4.24}$$

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:

$$mass\, of\, ethyl\, acetate = moleethyl\, acetate \times molar\, mass\, ethyl\, acetate \tag{4.4.25}$$

$$= 0.171\, mol\, CH_3CO_2C_2H_5 \times \frac{88.11\, g\, CH_3CO_2C_2H_5}{1\, mol\, CH_3CO_2C_2H_5} \tag{4.4.26}$$

$$= 15.1\, g\, CH_3CO_2C_2H_5 \tag{4.4.27}$$

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:

$$volume\, of\, ethyl\, acetate = 15.1\, g\, CH_3CO_2C_2H_5 \times \frac{1\, ml\, CH_3CO_2C_2H_5}{0.9003\, g\, CH_3CO_2C_2H_5} \tag{4.4.28}$$

$$= 16.8\, ml\, CH_3CO_2C_2H_5 \tag{4.4.29}$$

Exercise 4.4.1

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: 35.9 g

Limiting Reactants in Solutions

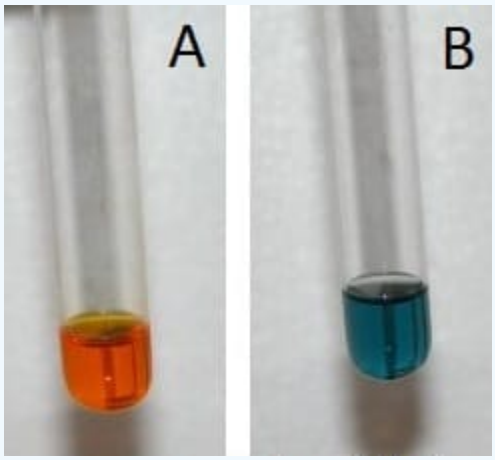
The concept of limiting reactants applies to reactions carried out in solution as well as to reactions involving pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example 4.4.2.

Example

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:

$$3CH_3CH_2OH(aq) + \underset{yellow-orange}{2Cr_2O_7^{2-}}(aq) + 16H^+(aq) \xrightarrow[H_2SO_4(aq)]{Ag^+} 3CH_3CO_2H(aq) + \underset{green}{4Cr^{3+}}(aq) + 11H_2O(l) \tag{4.4.30}$$

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. **U**se 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

$$moles\ of\ C_2H_5OH = (2.6 \times 10^{-6}\ \cancel{mol\ Cr_2O_7^{2-}})\left(\frac{3\ mol\ C_2H_5OH}{2\ \cancel{mol\ Cr_2O_7^{2-}}}\right) = 3.9 \times 10^{-6}\ mol\ C_2H_5OH$$

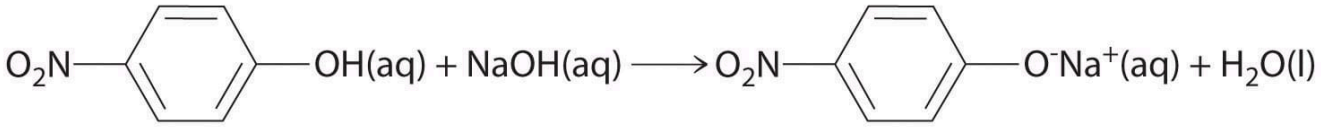
As indicated in the strategy, this number can be converted to the mass of C_2H_5OH using its molar mass:

$$mass\ C_2H_5OH = (3.9 \times 10^{-6}\ \cancel{mol\ C_2H_5OH})\left(\frac{46.07\ g}{\cancel{mol\ C_2H_5OH}}\right) = 1.8 \times 10^{-4}\ g\ C_2H_5OH$$

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 4.4.2

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**

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: 4.93×10^{-5} L or 49.3 µL

In Examples 4.4.1 and 4.4.2, 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 4.4.3.

Example 4.4.3

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:

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq)$$

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 4.4.2). The first step is to calculate the number of moles of each reactant in the specified volumes:

$$moles\ K_2Cr_2O_7 = 500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.17\ mol\ K_2Cr_2O_7}{1\ \cancel{L}}\right) = 0.085\ mol\ K_2Cr_2O_7 \tag{4.4.31}$$

$$moles\ AgNO_3 = 250\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.57\ mol\ AgNO_3}{1\ \cancel{L}}\right) = 0.14\ mol\ AgNO_3 \tag{4.4.32}$$

B Now determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

$$K_2Cr_2O_7:\ \frac{0.085\ mol}{1\ mol} = 0.085 \tag{4.4.33}$$

$$AgNO_3:\ \frac{0.14\ mol}{2\ mol} = 0.070 \tag{4.4.34}$$

Because 0.070 < 0.085, we know that $AgNO_3$ is the limiting reactant.

C Each mole of $Ag_2Cr_2O_7$ formed requires 2 mol of the limiting reactant ($AgNO_3$), so we can obtain only 0.14/2 = 0.070 mol of $Ag_2Cr_2O_7$. Finally, convert the number of moles of $Ag_2Cr_2O_7$ to the corresponding mass:

$$mass\ of\ Ag_2Cr_2O_7 = 0.070\ \cancel{mol}\left(\frac{431.72\ g}{1\ \cancel{mol}}\right) = 30\ g\ Ag_2Cr_2O_7 \tag{4.4.35}$$

The Ag^+ and $Cr_2O_7^{2-}$ ions form a red precipitate of solid $Ag_2Cr_2O_7$, while the K^+ and NO_3^- ions remain in solution. (Water molecules are omitted from molecular views of the solutions for clarity.)

Exercise 4.4.3

Aqueous solutions of sodium bicarbonate and sulfuric acid react to produce carbon dioxide according to the following equation:

$$2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow 2CO_2(g) + Na_2SO_4(aq) + 2H_2O(l)$$

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: 3.4 g

YouTube Video

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Limiting Reactant Problems Using Molarities: https://youtu.be/eOXTliL-gNw

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.

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4.5: Other Practical Matters in Reaction Stoichiometry

Learning Objectives

- To understand the concept of quantify incomplete reactions, including sequential and parallel reactions.

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:

$$percent\,yield = \frac{actual\,yield\,(g)}{theoretical\,yield\,(g)} \times 100 \tag{4.5.1}$$

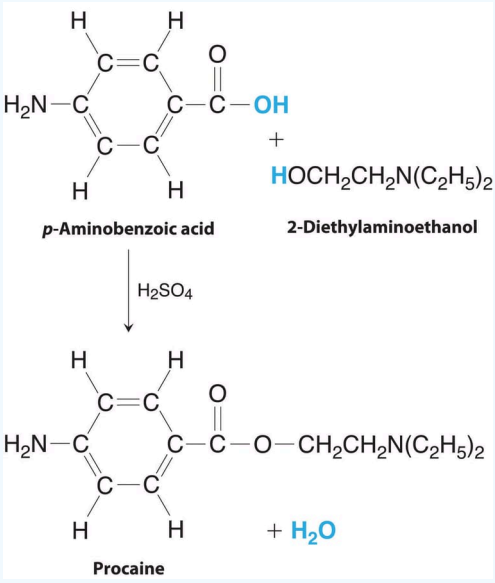
The method used to calculate the percent yield of a reaction is illustrated in Example 4.5.1.

Example 4.5.1: 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

$$\underset{p-aminobenzoic\,acid}{C_7H_7NO_2} + \underset{2-diethylaminoethanol}{C_6H_{15}NO} \xrightarrow{H_2SO_4} \underset{procaine}{C_{13}H_{20}N_2O_2} + H_2O \tag{4.5.1}$$

If this reaction was carried out using 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:

$$moles\, p-aminobenzoic\, acid = 10.0\, g \times \frac{1\, mol}{137.14\, g} = 0.0729\, mol\, p-aminbenzoic\, acid \tag{4.5.2}$$

$$moles\, 2-diethylaminoethanol = 10.0\, g \times \frac{1\, mol}{117.19\, g} = 0.0853\, mol\, 2-diethylaminoethanol \tag{4.5.3}$$

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.

$$theoretical\, yield\, of\, procaine = 0.0729\, mol \times \frac{236.31\, g}{1\, mol} = 17.2\, g \tag{4.5.4}$$

C The actual yield was only 15.7 g of procaine, so the percent yield is

$$percent\, yield = \frac{15.7\, g}{17.2\, g} \times 100 = 91.3\% \tag{4.5.5}$$

(If the product were pure and dry, this yield would indicate very good lab technique!)

Exercise 4.5.1: 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:

$$2PbS_{(s)} + 3O_2 \rightarrow 2PbO_{(s)} + 2SO_{2(g)} \tag{4.5.6}$$

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:

$$PbO_{(s)} + C_{(s)} \rightarrow Pb_{(l)} + CO_{(g)} \tag{4.5.7}$$

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?



Figure used with permission from Wikipedia.

Answer: 89.2%

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.

Consecutive Reactions, Simultaneous Reactions, and Overall Reactions

Most of time it takes more than one steps to get desired product. Two more complex reactions are the consecutive and simultaneous reactions. Reactions that are carried out one after another in sequence to yield a final product are called consecutive reactions (e.g., occurring sequenceally):

$$A \rightarrow Y \rightarrow Z \tag{4.5.2}$$

Any substance that is produced in one step and is consumed in another step of a multistep process is called an *intermediate* (e.g., Y in Equation 4.5.2). The *Overall Reaction* is the chemical equation that expresses all the reactions occurring in a single overall equation.

Example $4.5.2$:Purification of TiO_2

Step 1:

$$2TiO2_{(\text{impure solid})} + 3C_{(s)} + 4Cl_{2(g)} \rightarrow 2TiCl_{4(g)} + CO_{2(g)} + 2CO_{(g)} \tag{4.5.8}$$

Step 2:

$$2 \times [TiCl_{4(g)} + O_{2(g)} \rightarrow TiO_{2(s)} + 2Cl_{2(g)}] \tag{4.5.9}$$

Overall:

$$3C_{(s)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2CO_{(g)} \tag{4.5.10}$$

$TiCl_4$ is an intermediate in this reaction

Example 4.5.3

How many gram of $NaBr$ is produced if 55.85g of Fe is consumed the the following series of reactions?

$$3Fe + 3Br_2 \rightarrow 3FeBr_2 \tag{4.5.11}$$

$$3FeBr_2 + Br_2 \rightarrow Fe_3Br_8 \tag{4.5.12}$$

$$Fe_3Br_8 + 4Na_2CO_3 \rightarrow 8NaBr + 4CO_2 + Fe_3O_4 \tag{4.5.13}$$

Overall reaction:

$$3Fe + 4Br_2 + 4Na_2CO_3 \rightarrow 8NaBr + 4CO_2 + Fe_3O_4 \tag{4.5.14}$$

Solution

under construction

In simultaneous reactions, two or more substances react independently of one another in separate reactions occurring simultaneously

$$A \rightarrow Y \tag{4.5.3a}$$

and

$$B \rightarrow B \tag{4.5.3b}$$

Equations 4.5.3 involve two reactions evolving in parallel, however sometimes there exist a coupling between the two (or more) reactions with shared reactant, intermediates or products. is competition involved, like in the scheme:

$$A + B \rightarrow Y \tag{4.5.4a}$$

and

$$A + C \rightarrow Z \tag{4.5.3b}$$

In the above simultaneous reaction, both B and C compete with each another for reacting A. This is superficially similar to a common ion effect.

Example 4.5.4: Oxidation of Magnalium

Magnalium is an aluminum alloy with magnesium that exhibits greater strength, greater corrosion resistance, and lower density than pure aluminum. How many grams of $H_{2(g)}$ are generated if a 0.710 g piece of magnalium (with a 70% Al and 30.0% Mg by mass composition) with excess $HCl_{(aq)}$?

Solution

under construction

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.

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5: INTRODUCTION TO REACTIONS IN AQUEOUS SOLUTIONS

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

5.1: The Nature of Aqueous Solutions
5.2: Precipitation Reactions
5.3: Acid-Base Reactions
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5.1: The Nature 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 5.1.1, 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 5.1.1). Because of the arrangement of polar bonds in a water molecule, water is described as a polar substance.

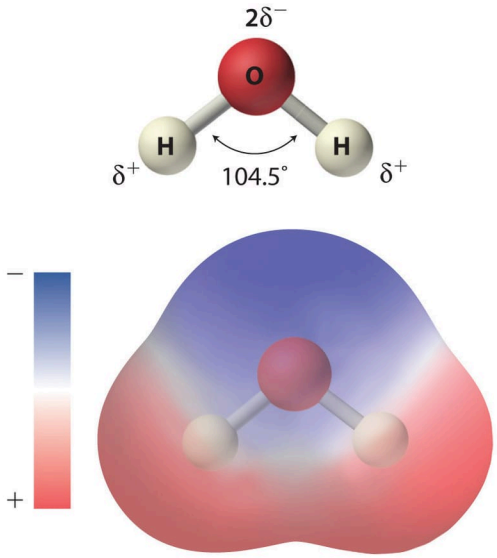


Figure 5.1.1: The Polar Nature of Water. *Each water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. Because the oxygen atom attracts electrons more strongly than the hydrogen atoms do, the oxygen atom is partially negatively charged ($2\delta^-$; blue) 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.*

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 5.1.2). 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!

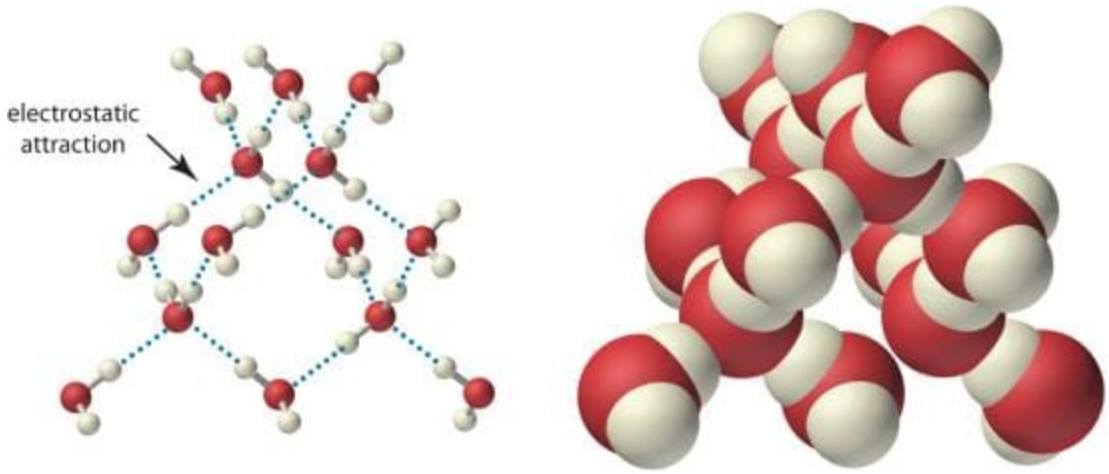


Figure 5.1.2: The Structure of Liquid Water. Two views of a water molecule are shown: (a) a ball-and-stick structure and (b) a space-filling model. Water molecules are held together by electrostatic attractions (dotted lines) between the partially negatively charged oxygen atom of one molecule and the 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.

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 5.1.3). 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

$$NaCl(s) \xrightarrow{H_2O(l)} Na^+(aq) + Cl^-(aq)$$

where (aq) indicates that Na^+ and Cl^- are hydrated ions.

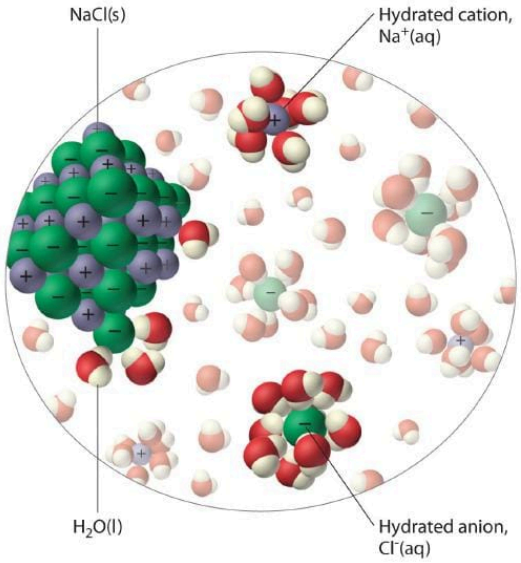


Figure 5.1.3: The Dissolution of Sodium Chloride in Water. *An ionic solid such as sodium chloride dissolves in water because of the electrostatic attraction between the cations (Na^+) and the partially negatively charged oxygen atoms of water molecules, and between the anions (Cl^-) and the partially positively charged hydrogen atoms of water.*

Note

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 $5.1.4$). 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 $5.1.4$ 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.

Note

Solutions that contain ions conduct electricity.

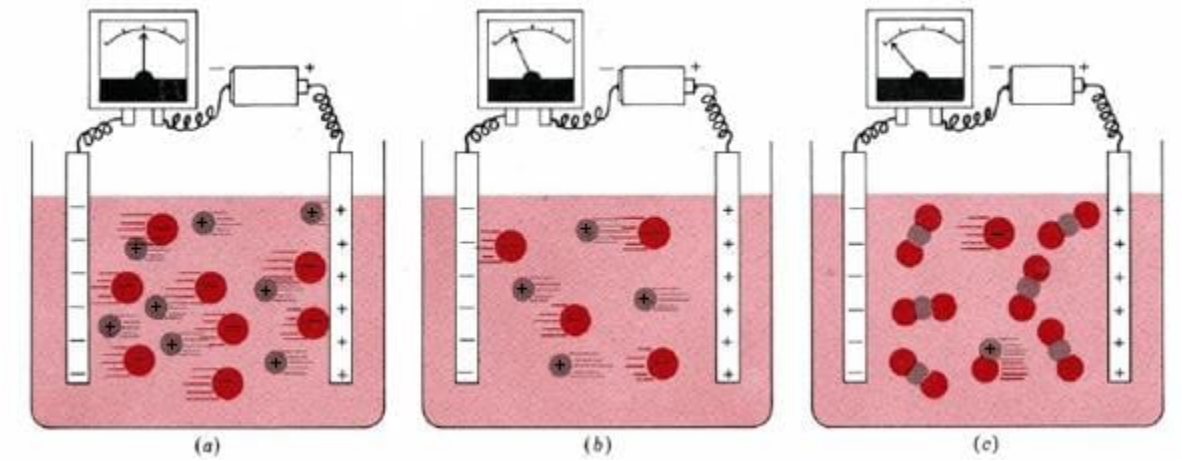


Figure used with permission from ChemePrime.

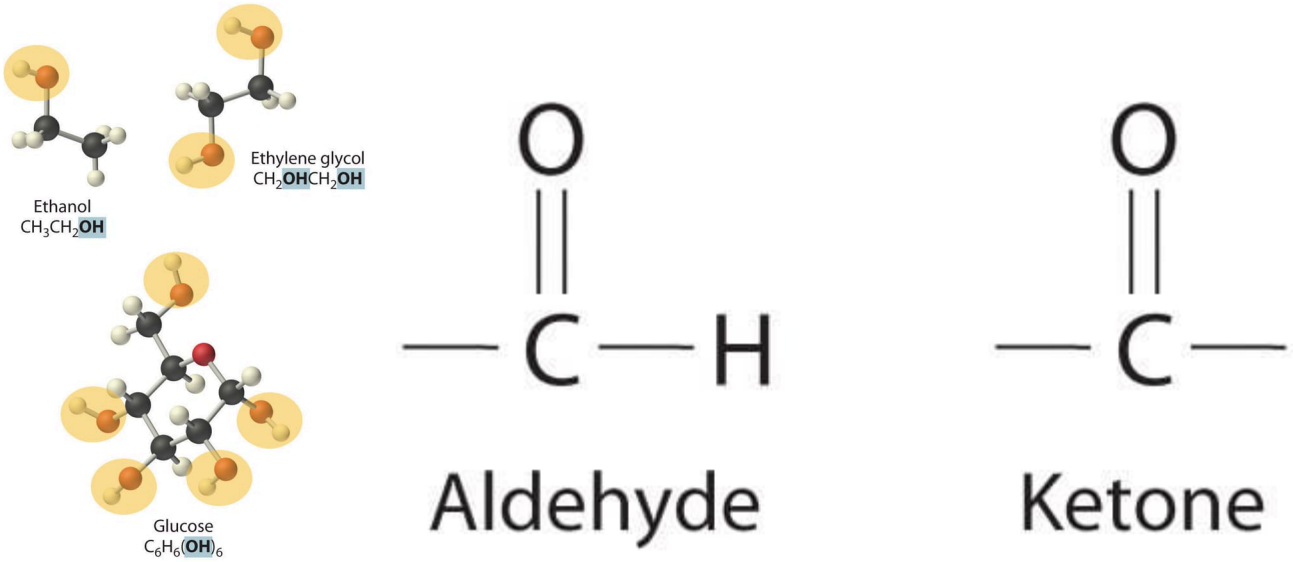
An electrolyte is any compound that can form ions when dissolved in water (c.f. nonelectrolytes). Electrolytes may be strong or weak. is any compound that can form ions when it dissolves in water. When strong electrolytes dissolve, the constituent ions dissociate completely due to strong electrostatic interactions with the solvent, producing aqueous solutions that conduct electricity very well (Figure $5.1.4$). Examples include ionic compounds such as barium chloride ($BaCl_2$) and sodium hydroxide (NaOH), which are both strong electrolytes and dissociate as follows:

$$BaCl_2(s) \xrightarrow{H_2O(l)} Ba^{2+}(aq) + 2Cl^-(aq)$$

$$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$$

The single arrows from reactant to products in Equation 5.1.2 and Equation 5.1.3 indicate that dissociation is **complete**.

When weak electrolytes dissolve, they produce relatively few ions in solution. This does *not* 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 elsewhere.



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. 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 5.1.5.

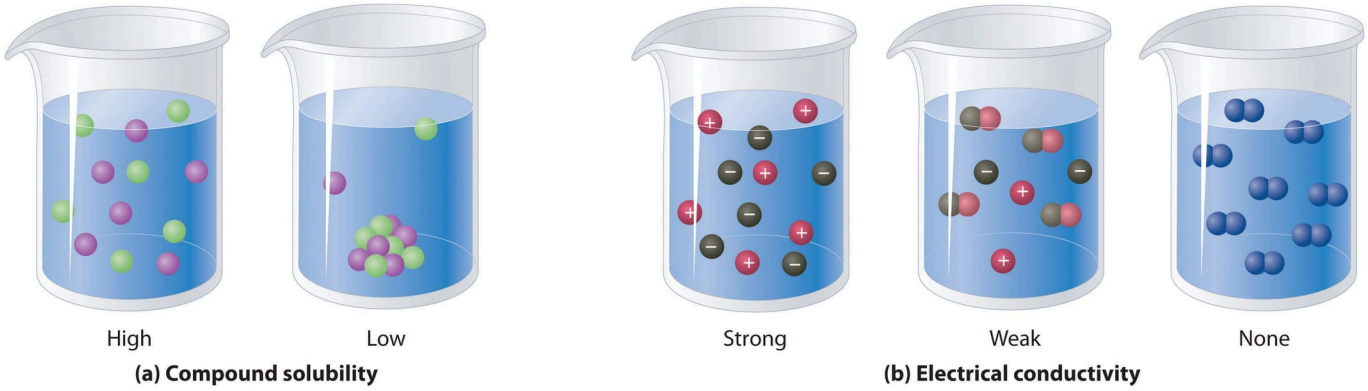


Figure 5.1.5: The Difference between Soluble and Insoluble Compounds (a) and Strong, Weak, and Nonelectrolytes (b). *When a soluble compound dissolves, its constituent atoms, molecules, or ions disperse throughout the solvent. In contrast, the constituents of an insoluble compound remain associated with 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.*

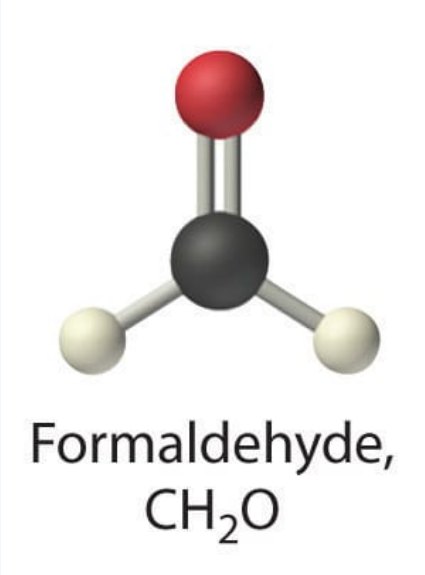
Note

Ionic substances and carboxylic acids are electrolytes; alcohols, aldehydes, and ketones are nonelectrolytes.

Example 5.1.1

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

a. formaldehyde



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.

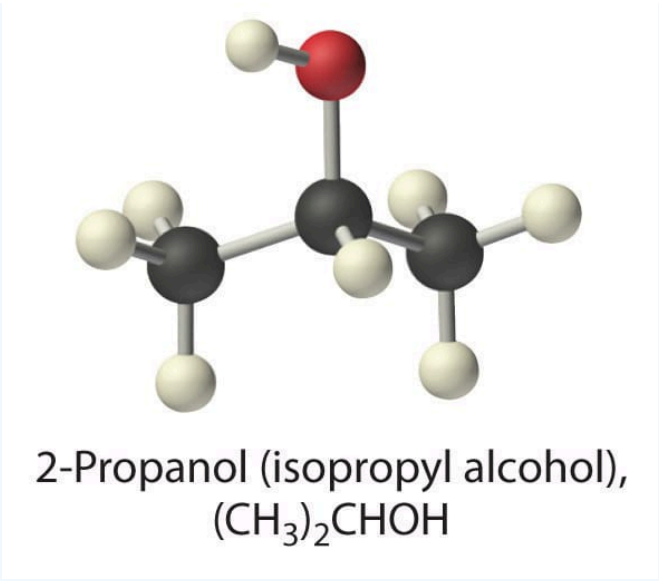
Solution:

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 5.1.1

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

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Predicting the Solubility of Ionic Compounds: https://youtu.be/U3QNwnfmvGU

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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Modified by Joshua Halpern (Howard University)

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5.2: Precipitation Reactions

Learning Objectives

- To identify a precipitation reaction and predict solubilities.

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:

$$AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + KNO_3(aq) \tag{5.2.1}$$

This equation has the general form of an exchange reaction:

$$AC + BD \rightarrow \underset{insoluble}{AD} + BC \tag{5.2.2}$$

Thus 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.

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***Video**: Mixing Potassium Chromate and Silver Nitrate together to initiate a precipitation reaction (Equation 5.2.3).*

While chemical equations show the identities of the reactants and the products and gave the stoichiometries of the reactions, but they told us very little about what was 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. 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:

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq) \tag{5.2.3}$$

Although Equation 5.2.3 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 $AgNO_3$ and $K_2Cr_2O_7$ are strong electrolytes, they dissociate completely in aqueous solution to form ions. In contrast, because $Ag_2Cr_2O_7$ 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:

$$2Ag^+(aq) + 2NO_3^-(aq) + 2K^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2K^+(aq) + 2NO_3^-(aq) \tag{5.2.4}$$

Note that $K^+(aq)$ and $NO_3^-(aq)$ ions are present on both sides of the equation, 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:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{5.2.5}$$

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 5.2.5, the charge on the left side is 2(+1) + 1(−2) = 0, which is the same as the charge of a neutral $Ag_2Cr_2O_7$ formula unit.

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:

$$2AgF(aq) + (NH_4)_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4F(aq) \tag{5.2.6}$$

The complete ionic equation for this reaction is as follows:

$$2Ag^+(aq) + 2F^-(aq) + 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4^+(aq) + 2F^-(aq) \tag{5.2.7}$$

Because two NH_4^+(aq) and two F^-(aq) ions appear on both sides of Equation 5.2.7, they are spectator ions. They can therefore be canceled to give the net ionic equation (Equation 5.2.8), which is identical to Equation 5.2.5:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{5.2.8}$$

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.

Example 5.2.1

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:

$$Ba(NO_3)_2(aq) + Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + NaNO_3(aq)$$

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:

$$3Ba(NO_3)_2(aq) + 2Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + 6NaNO_3(aq)$$

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:

$$3Ba^{2+}(aq) + 6NO_3^-(aq) + 6Na^+(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s) + 6Na^+(aq) + 6NO_3^-(aq)$$

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:

$$3Ba^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s)$$

Exercise 5.2.1: 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

overall chemical equation:

$$3AgF(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + 3NaF(aq)$$

complete ionic equation:

$$3Ag^+(aq) + 3F^-(aq) + 3Na^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s) + 3Na^+(aq) + 3F^-(aq)$$

net ionic equation:

$$3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s)$$

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.

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Determining the Products for Precipitation Reactions: https://youtu.be/r0kYeZVuTAM

Predicting Solubilities

Table 5.2.2 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 5.2.2 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 5.2.2: 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 5.2.1).

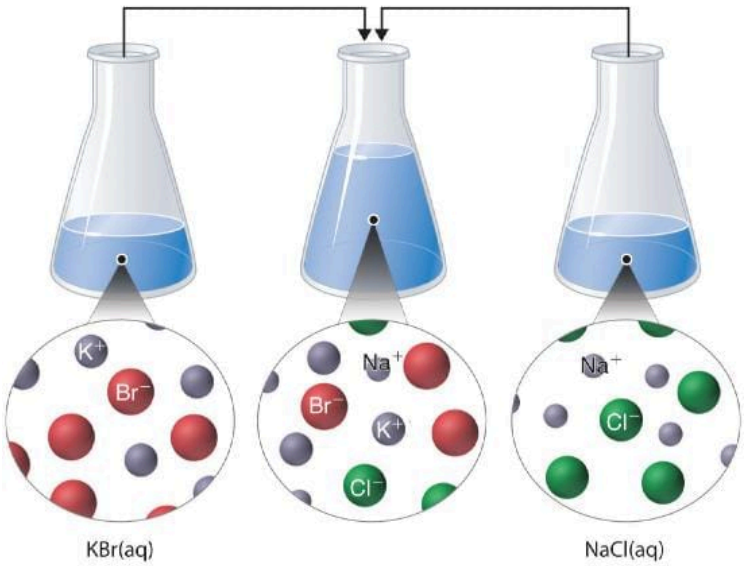


Figure 5.2.1: The Effect of Mixing Aqueous KBr and NaCl Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

Example 5.2.2

Using the information in Table 5.2.2, 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

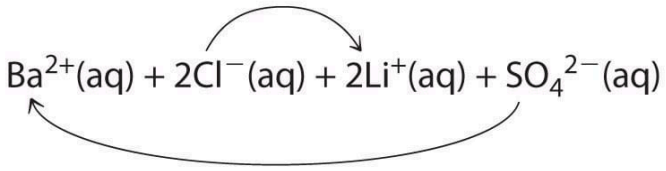
Asked for: reaction and net ionic equation

Strategy:

A. Identify the ions present in solution and write the products of each possible exchange reaction.
B. Refer to Table 5.2.2 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 5.2.2 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

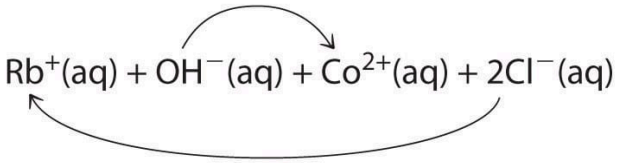
$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) \tag{5.2.9}$$

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.

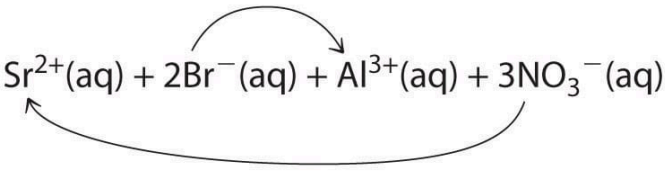
1. **A** Rubidium hydroxide and cobalt(II) chloride are strong electrolytes, so when aqueous solutions of these compounds are mixed, the resulting solution initially contains Rb^+, OH^-, Co^{2+}, and Cl^- ions. The possible products of an exchange reaction are rubidium chloride and cobalt(II) hydroxide):



B According to Table $5.2.2$, 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:

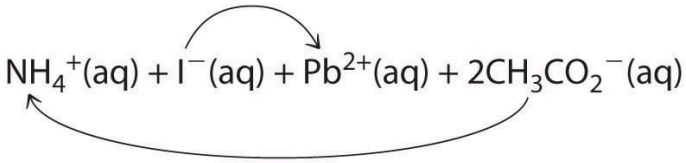
$$Co^{2+}(aq) + 2OH^-(aq) \rightarrow Co(OH)_2(s)$$

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 $5.2.2$, 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 $5.2.2$, 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 5.2.2, 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 5.2.2

Using the information in Table 5.2.2, 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. $Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_2(s)$
b. $2PO_4^{3-}(aq) + 3Hg^{2+}(aq) \rightarrow Hg_3(PO_4)_2(s)$
c. $NaF(s)$ dissolves; no net reaction
d. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

Precipitation Reactions in Photography

Precipitation reactions can be used to recover silver from solutions used to develop conventional photographic film. Although largely supplanted by digital photography, conventional methods are often used for artistic purposes. Silver bromide is an off-white solid that turns black when exposed to light, which is due to the formation of small particles of silver metal. Black-and-white photography uses this reaction to capture images in shades of gray, with the darkest areas of the film corresponding to the areas that received the most light. The first step in film processing is to enhance the black/white contrast by using a developer to increase the amount of black. The developer is a reductant: because silver atoms catalyze the reduction reaction, grains of silver bromide that have already been partially reduced by exposure to light react with the reductant much more rapidly than unexposed grains.

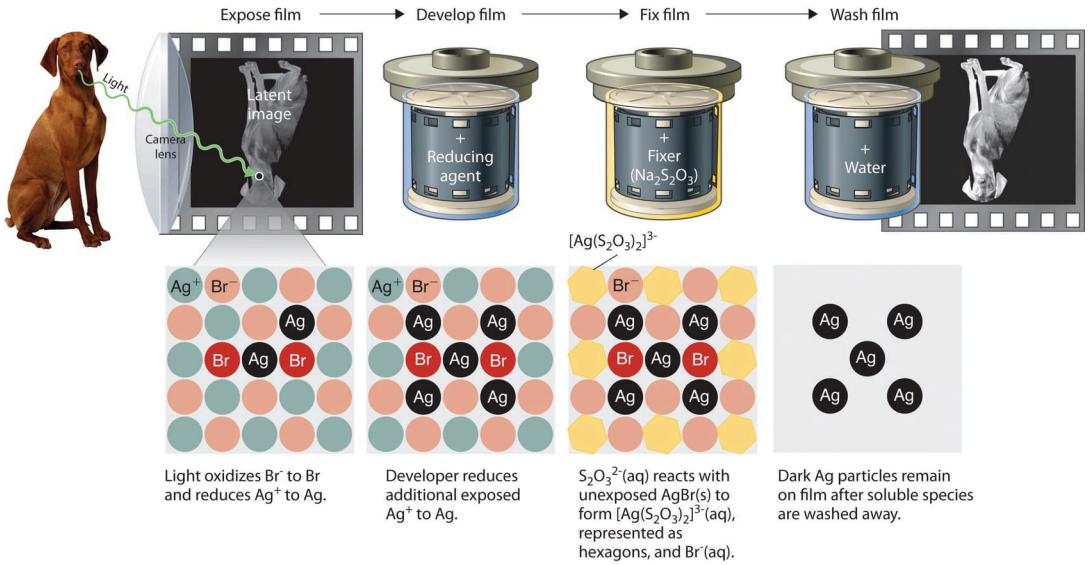


Figure 5.2.2: Outline of the Steps Involved in Producing a Black-and-White Photograph

After the film is developed, any unexposed silver bromide must be removed by a process called "fixing"; otherwise, the entire film would turn black with additional exposure to light. Although silver bromide is insoluble in water, it is soluble in a dilute solution of sodium thiosulfate ($Na_2S_2O_3$; *photographer's hypo*) because of the formation of $[Ag(S_2O_3)_2]^{3-}$ ions. Thus washing the film with thiosulfate solution dissolves unexposed silver bromide and leaves a pattern of metallic silver granules that constitutes the negative. This procedure is summarized in Figure 5.2.2. The negative image is then projected onto paper coated with silver halides, and the developing and fixing processes are repeated to give a positive image. (Color photography works in much the same way, with a combination of silver halides and organic dyes superimposed in layers.) "Instant photo" operations can generate more than a hundred gallons of dilute silver waste solution per day. Recovery of silver from thiosulfate fixing solutions involves first removing the thiosulfate by oxidation and then precipitating Ag^+ ions with excess chloride ions.

Example 5.2.3

A silver recovery unit can process 1500 L of photographic silver waste solution per day. Adding excess solid sodium chloride to a 500 mL sample of the waste (after removing the thiosulfate as described previously) gives a white precipitate that, after filtration and drying, consists of 3.73 g of AgCl. What mass of NaCl must be added to the 1500 L of silver waste to ensure that all the Ag^+ ions precipitate?

Given: volume of solution of one reactant and mass of product from a sample of reactant solution

Asked for: mass of second reactant needed for complete reaction

Strategy:

A. Write the net ionic equation for the reaction. Calculate the number of moles of AgCl obtained from the 500 mL sample and then determine the concentration of Ag^+ in the sample by dividing the number of moles of AgCl formed by the volume of solution.

B. Determine the total number of moles of Ag^+ in the 1500 L solution by multiplying the Ag^+ concentration by the total volume.

C. Use mole ratios to calculate the number of moles of chloride needed to react with Ag^+. Obtain the mass of NaCl by multiplying the number of moles of NaCl needed by its molar mass.

Solution:

We can use the data provided to determine the concentration of Ag^+ ions in the waste, from which the number of moles of Ag^+ in the entire waste solution can be calculated. From the net ionic equation, we can determine how many moles of Cl^- are needed, which in turn will give us the mass of NaCl necessary.

A The first step is to write the net ionic equation for the reaction:

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$

We know that 500 mL of solution produced 3.73 g of AgCl. We can convert this value to the number of moles of AgCl as follows:

$$moles\ AgCl = \frac{grams\ AgCl}{molar\ mass\ AgCl} = 3.73\ \cancel{g\ AgCl}\left(\frac{1\ mol\ AgCl}{143.32\ \cancel{g\ AgCl}}\right) = 0.0260\ mol\ AgCl \tag{5.2.10}$$

Therefore, the 500 mL sample of the solution contained 0.0260 mol of Ag^+. The Ag^+ concentration is determined as follows:

$$[Ag^+] = \frac{moles\ Ag^+}{liters\ soln} = \frac{0.0260\ mol\ AgCl}{0.500\ L} = 0.0520\ M \tag{5.2.11}$$

B The total number of moles of Ag^+ present in 1500 L of solution is as follows:

$$moles\ Ag^+ = 1500\ \cancel{L}\left(\frac{0.520\ mol}{1\ \cancel{L}}\right) = 78.1\ mol\ Ag^+ \tag{5.2.12}$$

C According to the net ionic equation, one Cl^- ion is required for each Ag^+ ion. Thus 78.1 mol of NaCl are needed to precipitate the silver. The corresponding mass of NaCl is

$$mass\ NaCl = 78.1\ \cancel{mol\ NaCl}\left(\frac{58.44\ g\ NaCl}{1\ \cancel{mol\ NaCl}}\right) = 4560\ g\ NaCl = 4.56\ kg\ NaCl \tag{5.2.13}$$

Note that 78.1 mol of AgCl correspond to 8.43 kg of metallic silver, which is worth about $7983 at 2011 prices ($32.84 per troy ounce). Silver recovery may be economically attractive as well as ecologically sound, although the procedure outlined is becoming nearly obsolete for all but artistic purposes with the growth of digital photography.

Exercise 5.2.3

Because of its toxicity, arsenic is the active ingredient in many pesticides. The arsenic content of a pesticide can be measured by oxidizing arsenic compounds to the arsenate ion (AsO_4^{3-}), which forms an insoluble silver salt (Ag_3AsO_4). Suppose you are asked to assess the purity of technical grade sodium arsenite ($NaAsO_2$), the active ingredient in a pesticide used against termites. You dissolve a 10.00 g sample in water, oxidize it to arsenate, and dilute it with water to a final volume of 500 mL. You then add excess $AgNO_3$ solution to a 50.0 mL sample of the arsenate solution. The resulting precipitate of Ag_3AsO_4 has a mass of 3.24 g after drying. What is the percentage by mass of $NaAsO_2$ in the original sample?

Answer: 91.0%

Note

Precipitation reactions are a subclass of double displacement reactions.

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Determining the Net Ionic Equation for a Precipitation Reaction: https://youtu.be/AMJz1Sdz8IA

Summary

A complete ionic equation consists of the net ionic equation and spectator ions. Predicting the solubility of ionic compounds in water can give insight into whether or not a reaction will occur. The chemical equation for a reaction in solution can be written in three ways. The **overall chemical equation** shows all the substances present in their undissociated forms; the **complete ionic equation** shows all the substances present in the form in which they actually exist in solution; and the **net ionic equation** is derived from the complete ionic equation by omitting all **spectator ions**, ions that occur on both sides of the equation with the same coefficients. Net ionic equations demonstrate that many different combinations of reactants can give the same net chemical reaction.

In a **precipitation reaction**, a subclass of exchange reactions, an insoluble material (a **precipitate**) forms when solutions of two substances are mixed. To predict the product of a precipitation reaction, all species initially present in the solutions are identified, as are any combinations likely to produce an insoluble salt.

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5.3: Acid-Base Reactions

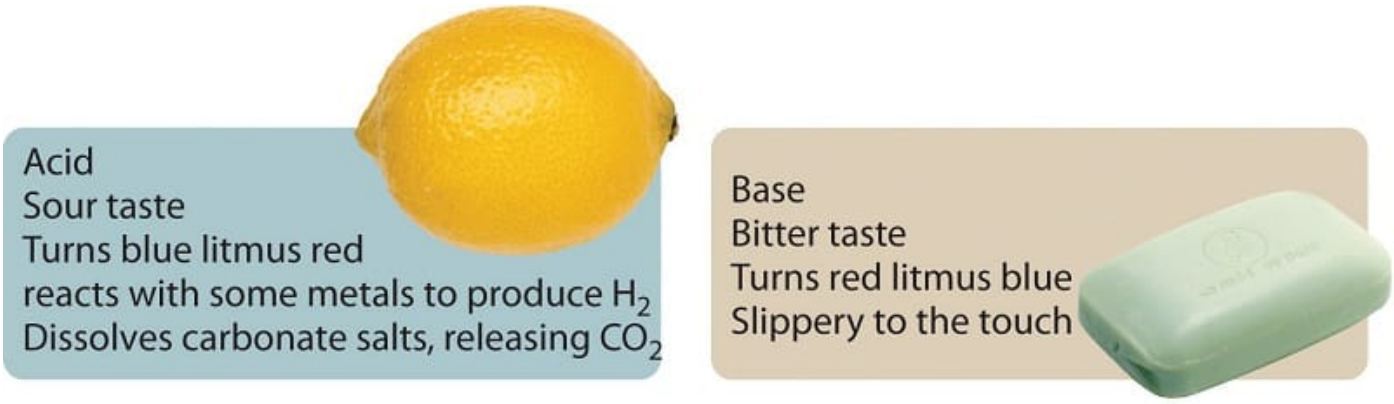
Learning Objectives

- 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 defined **acids** as substances that dissolve in water to produce H^+ ions, whereas **bases** were 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.



Although we include their tastes among the common characteristics of acids and bases, we never advocate tasting an unknown chemical!

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 5.3.1), and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide (OH^-) ions (Equation 5.3.2):

$$\underset{\text{an Arrhenius acid}}{HCl_{(g)}} \xrightarrow{H_2O_{(l)}} H^+_{(aq)} + Cl^-_{(aq)} \tag{5.3.1}$$

$$\underset{\text{an Arrhenius base}}{NaOH_{(s)}} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + OH^-_{(aq)} \tag{5.3.2}$$

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 5.3.3) is not an acid–base reaction because it does not involve H^+ and OH^-:

$$NH_{3\ (g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)} \tag{5.3.3}$$

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 5.3.3, 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.

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Definitions of Acids and Bases: https://youtu.be/r8reN0CSIHw

Polyprotic Acids

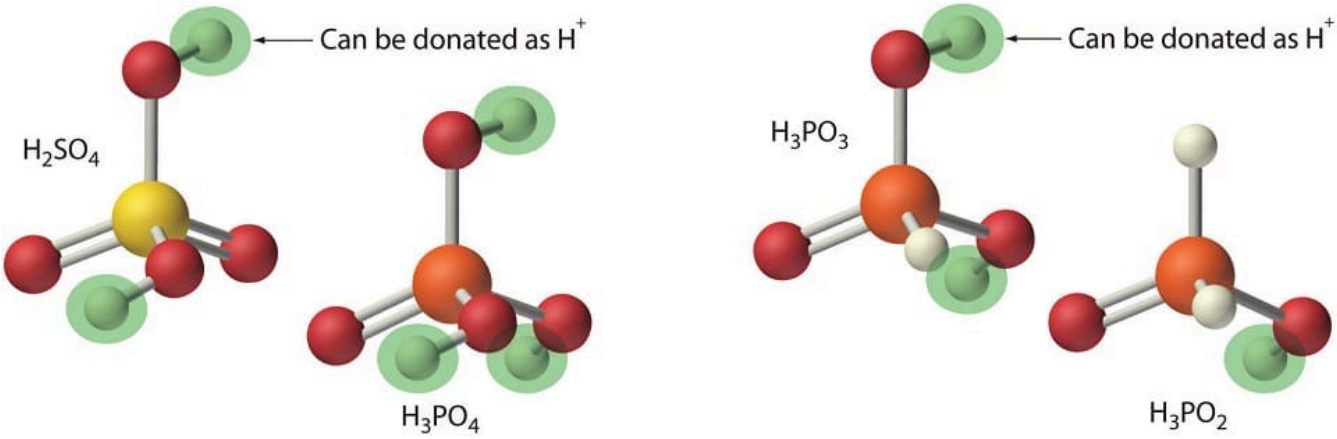
Acids differ in the number of protons they can donate. For example, monoprotic acids (a compound that is capable of donating one proton per molecule) are compounds that are capable of donating a single proton per molecule. Monoprotic acids include HF, HCl, HBr, HI, HNO_3, and HNO_2. All carboxylic acids 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. can donate more than one proton per molecule. 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), (Equations 5.3.4, 5.3.5, and 5.3.6):

$$H_3PO_4(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + H_2PO_4^-(aq) \tag{5.3.4}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \tag{5.3.5}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \tag{5.3.6}$$

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).



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 (An acid that reacts essentially completely with water) to give H^+ and the corresponding anion. react essentially completely with water to give H^+ and the corresponding anion. Similarly, strong bases (A base that dissociates essentially completely in water) to give OH^- and the corresponding cation) 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 (An acid in which only a fraction of the molecules react with water) to producee H^+ and the corresponding anion. and weak bases (A base in which only a fraction of the molecules react with water to produce OH^- and the corresponding cation) 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:

$$CH_3CO_2H(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + CH_3CO_2^-(aq) \tag{5.3.7}$$

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), as we stated in section 8.1. Sulfuric acid is unusual in that it is a strong acid when it donates its first proton (Equation 5.3.8) but a weak acid when it donates its second proton (Equation 5.3.9) as indicated by the single and double arrows, respectively:

$$\underset{strong\ acid}{H_2SO_4(l)} \xrightarrow{H_2O(l)} H^+(aq) + HSO_4^-(aq) \tag{5.3.8}$$

$$\underset{weak\ acid}{HSO_4^-(aq)} \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \tag{5.3.9}$$

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.

The most common weak base is ammonia, which reacts with water to form small amounts of hydroxide ion:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{5.3.10}$$

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.

Table 5.3.1 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 5.3.1: Common Strong Acids and Bases

Strong Acids		Strong Bases	
Hydrogen Halides	**Oxoacids**	**Group 1 Hydroxides**	**Hydroxides of the Heavier 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 5.3.1

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 5.3.7), 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 5.3.1 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 5.3.1

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. strong base
b. strong acid
c. weak acid
d. weak base
e. none of these; formaldehyde is a neutral molecule

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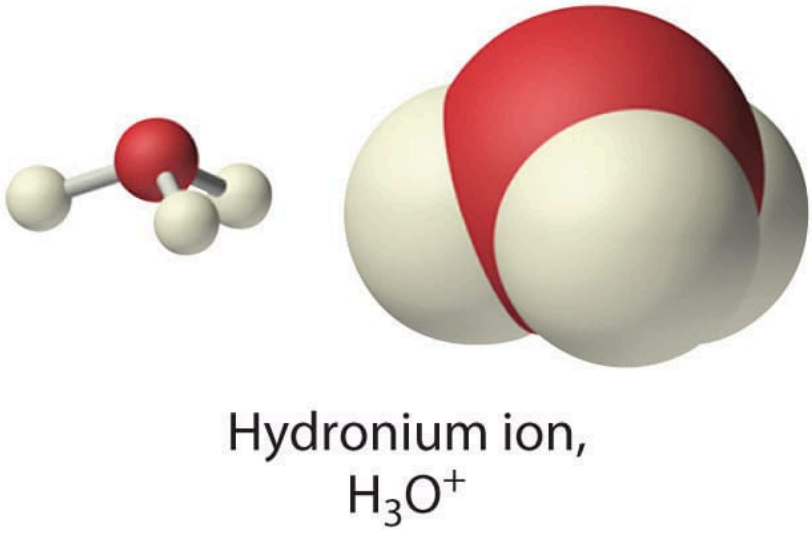
Definition of Strong/Weak Acids & Bases: https://youtu.be/gN2l8H_AWGU

The Hydronium Ion

Because isolated protons are *very* unstable and hence very reactive, an acid never simply "loses" an H^+ ion. Instead, the proton is always transferred to another substance, which acts as a base in the Brønsted–Lowry definition. Thus in every acid–base reaction, one species acts as an acid and one species acts as a base. Occasionally, the same substance performs both roles, as you will see later. When a strong acid dissolves in water, the proton that is released is transferred to a water molecule that acts as a proton acceptor or base, as shown for the dissociation of sulfuric acid:

$$\underset{\text{acid (proton donor)}}{H_2SO_4(l)} + \underset{\text{base (proton acceptor)}}{H_2O(l)} \rightarrow \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{HSO_4^-(aq)} \tag{5.3.11}$$

Technically, therefore, it is imprecise to describe the dissociation of a strong acid as producing $H^+_{(aq)}$ ions, as we have been doing. The resulting H_3O^+ ion, called the hydronium ion and is a more accurate representation of $H^+_{(aq)}$. For the sake of brevity, however, in discussing acid dissociation reactions, we often show the product as $H^+_{(aq)}$ (as in Equation 5.3.7) with the understanding that the product is actually the$H_3O^+_{(aq)}$ ion.



Conversely, bases that do not contain the hydroxide ion accept a proton from water, so small amounts of OH^- are produced, as in the following:

$$\underset{base}{NH_3(g)} + \underset{acid}{H_2O(l)} \rightleftharpoons \underset{acid}{NH_4^+(aq)} + \underset{base}{OH^-(aq)} \tag{5.3.12}$$

Again, the double arrow indicates that the reaction does not go to completion but rather reaches a state of equilibrium. In this reaction, water acts as an acid by donating a proton to ammonia, and ammonia acts as a base by accepting a proton from water. Thus water can act as either an acid or a base by donating a proton to a base or by accepting a proton from an acid. Substances that can behave as both an acid and a base are said to be amphotericWhen substances can behave as both an acid and a base..

The products of an acid–base reaction are also an acid and a base. In Equation 5.3.11, for example, the products of the reaction are the hydronium ion, here an acid, and the hydrogen sulfate ion, here a weak base. In Equation 5.3.12, the products are NH_4^+, an acid, and OH^-, a base. The product NH_4^+ is called the conjugate acid of the base NH_3, and the product OH^- is called the conjugate baseThe substance formed when a Brønsted–Lowry acid donates a proton. of the acid H_2O. Thus all acid–base reactions actually involve two conjugate acid–base pairs. All acid–base reactions involve two conjugate acid–base pairs, the Brønsted–Lowry acid and the base it forms after donating its proton, and the Brønsted–Lowry base and the acid it forms after accepting a proton.; in Equation 5.3.12, they are NH_4^+/NH_3 and H_2O/OH^-.

Neutralization Reactions

A neutralization reaction (a chemical reaction in which an acid and a base react in stoichiometric amounts to produce water and a salt) is one in which an acid and a base react in stoichiometric amounts to produce water and a salt (the general term for any ionic substance that does not have OH– as the anion or H+ as the cation), the general term for any ionic substance that does not have OH^- as the anion or H^+ as the cation. If the base is a metal hydroxide, then the general formula for the reaction of an acid with a base is described as follows: *Acid plus base yields water plus salt*. For example, the reaction of equimolar amounts of HBr and NaOH to give water and a salt (NaBr) is a neutralization reaction:

$$\underset{acid}{HBr(aq)} + \underset{base}{NaOH(aq)} \rightarrow \underset{water}{H_2O(l)} + \underset{salt}{NaBr(aq)} \tag{5.3.13}$$

Acid plus base yields water plus salt.

If we write the complete ionic equation for the reaction in Equation 5.3.13, we see that $Na^+_{(aq)}$ and $Br^-_{(aq)}$ are spectator ions and are not involved in the reaction:

$$H^+(aq) + \cancel{Br^-(aq)} + \cancel{Na^+(aq)} + OH^-(aq) \rightarrow H_2O(l) + \cancel{Na^+(aq)} + \cancel{Br^-(aq)} \tag{5.3.14}$$

The overall reaction is therefore simply the combination of H^+(aq) and OH^-(aq) to produce H_2O, as shown in the net ionic equation:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \tag{5.3.15}$$

The net ionic equation for the reaction of any strong acid with any strong base is identical to Equation 5.3.15.

The strengths of the acid and the base generally determine whether the reaction goes to completion. The reaction of *any* strong acid with *any* strong base goes essentially to completion, as does the reaction of a strong acid with a weak base, and a weak acid with a strong base. Examples of the last two are as follows:

$$\underset{strong\ acid}{HCl(aq)} + \underset{weak\ base}{NH_3(aq)} \rightarrow \underset{salt}{NH_4Cl(aq)} \tag{5.3.16}$$

$$\underset{weak\ acid}{CH_3CO_2H(aq)} + \underset{strong\ base}{NaOH(aq)} \rightarrow \underset{salt}{CH_3CO_2Na(aq)} + H_2O(l) \tag{5.3.17}$$

Sodium acetate is written with the organic component first followed by the cation, as is usual for organic salts. Most reactions of a weak acid with a weak base also go essentially to completion. One example is the reaction of acetic acid with ammonia:

$$\underset{weak\ acid}{CH_3CO_2H(aq)} + \underset{weak\ base}{NH_3(aq)} \rightarrow \underset{salt}{CH_3CO_2NH_4(aq)} \tag{5.3.18}$$

An example of an acid–base reaction that does not go to completion is the reaction of a weak acid or a weak base with water, which is both an extremely weak acid and an extremely weak base.

Note

Except for the reaction of a weak acid or a weak base with water, acid–base reactions essentially go to completion.

In some cases, the reaction of an acid with an anion derived from a weak acid (such as HS^-) produces a gas (in this case, H_2S). Because the gaseous product escapes from solution in the form of bubbles, the reverse reaction cannot occur. Therefore, these reactions tend to be forced, or driven, to completion. Examples include reactions in which an acid is added to ionic compounds that contain the HCO_3^-, CN^-, or S^{2-} anions, all of which are driven to completion:

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq) \tag{5.3.19}$$

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l) \tag{5.3.20}$$

$$CN^-(aq) + H^+(aq) \rightarrow HCN(g) \tag{5.3.21}$$

$$S^{2-}(aq) + H^+(aq) \rightarrow HS^-(aq) \tag{5.3.22}$$

$$HS^-(aq) + H^+(aq) \rightarrow H_2S(g) \tag{5.3.23}$$

The reactions in Equations 5.3.19-5.3.22 are responsible for the rotten egg smell that is produced when metal sulfides come in contact with acids.

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Acid/Base Neutralization Reactions & Net Ionic Equations: https://youtu.be/gDS93ySeF80

Example 5.3.2: Calcium Propionate

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($CH_3CH_2CO_2H$) with aqueous calcium hydroxide [$Ca(OH)_2$] to give calcium propionate. Do you expect this reaction to go to completion, making it a feasible method for the preparation of calcium propionate?

Given: reactants and product

Asked for: balanced chemical equation and whether the reaction will go to completion

Strategy

Write the balanced chemical equation for the reaction of propionic acid with calcium hydroxide. Based on their acid and base strengths, predict whether the reaction will go to completion.

Solution

Propionic acid is an organic compound that is a weak acid, and calcium hydroxide is an inorganic compound that is a strong base. The balanced chemical equation is as follows:

$$2CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + 2H_2O(l)$$

The reaction of a weak acid and a strong base will go to completion, so it is reasonable to prepare calcium propionate by mixing solutions of propionic acid and calcium hydroxide in a 2:1 mole ratio.

Exercise 5.3.2

Write a balanced chemical equation for the reaction of solid sodium acetate with dilute sulfuric acid to give sodium sulfate.

Answer:

$$2CH_3CO_2Na(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CH_3CO_2H(aq)$$

One of the most familiar and most heavily advertised applications of acid–base chemistry is *antacids*, which are bases that neutralize stomach acid. The human stomach contains an approximately 0.1 M solution of hydrochloric acid that helps digest foods. If the protective lining of the stomach breaks down, this acid can attack the stomach tissue, resulting in the formation of an *ulcer*. Because one factor that is believed to contribute to the formation of stomach ulcers is the production of excess acid in the stomach, many individuals routinely consume large quantities of antacids. The active ingredients in antacids include sodium bicarbonate and potassium bicarbonate ($NaHCO_3$ and $KHCO_3$; Alka-Seltzer); a mixture of magnesium hydroxide and aluminum hydroxide [$Mg(OH)_2$ and $Al(OH)_3$; Maalox, Mylanta]; calcium carbonate ($CaCO_3$; Tums); and a complex salt, dihydroxyaluminum sodium carbonate [$NaAl(OH)_2CO_3$; original Rolaids]. Each has certain advantages and disadvantages. For example, $Mg(OH)_2$ is a powerful laxative (it is the active ingredient in milk of magnesia), whereas $Al(OH)_3$ causes constipation. When mixed, each tends

to counteract the unwanted effects of the other. Although all antacids contain both an anionic base (OH^-, CO_3^{2-}, or HCO_3^-) and an appropriate cation, they differ substantially in the amount of active ingredient in a given mass of product.



Stomach acid. An antacid tablet reacts with 0.1 M HCl (the approximate concentration found in the human stomach).

Example 5.3.3

Assume that the stomach of someone suffering from acid indigestion contains 75 mL of 0.20 M HCl. How many Tums tablets are required to neutralize 90% of the stomach acid, if each tablet contains 500 mg of $CaCO_3$? (Neutralizing all of the stomach acid is not desirable because that would completely shut down digestion.)

Given: volume and molarity of acid and mass of base in an antacid tablet

Asked for: number of tablets required for 90% neutralization

Strategy:

A. Write the balanced chemical equation for the reaction and then decide whether the reaction will go to completion.
B. Calculate the number of moles of acid present. Multiply the number of moles by the percentage to obtain the quantity of acid that must be neutralized. Using mole ratios, calculate the number of moles of base required to neutralize the acid.
C. Calculate the number of moles of base contained in one tablet by dividing the mass of base by the corresponding molar mass. Calculate the number of tablets required by dividing the moles of base by the moles contained in one tablet.

Solution:

A We first write the balanced chemical equation for the reaction:

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2CO_3(aq)$$

Each carbonate ion can react with 2 mol of H^+ to produce H_2CO_3, which rapidly decomposes to H_2O and CO_2. Because HCl is a strong acid and CO_3^{2-} is a weak base, the reaction will go to completion.

B Next we need to determine the number of moles of HCl present:

$$75 \ \cancel{mL} \left(\frac{1 \ \cancel{L}}{1000 \ \cancel{mL}} \right) \left(\frac{0.20 \ mol \ HCl}{\cancel{L}} \right) = 0.015 \ \ mol \ \ HCl$$

Because we want to neutralize only 90% of the acid present, we multiply the number of moles of HCl by 0.90:

$$(0.015\ mol\ HCl)(0.90) = 0.014\ mol\ HCl$$

We know from the stoichiometry of the reaction that each mole of $CaCO_3$ reacts with 2 mol of HCl, so we need

$$moles\ CaCO_3 = 0.014\ \cancel{mol\ HCl}\left(\frac{1\ mol\ CaCO_3}{2\ \cancel{mol\ HCl}}\right) = 0.0070\ mol\ CaCO_3$$

C Each Tums tablet contains

$$\left(\frac{500\ \cancel{mg\ CaCO_3}}{1\ Tums\ tablet}\right)\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg\ CaCO_3}}\right)\left(\frac{1\ mol\ CaCO_3}{100.1\ \cancel{g}}\right) = 0.00500\ mol\ CaCO_3$$

Thus we need $\dfrac{0.0070\ \cancel{mol\ CaCO_3}}{0.00500\ \cancel{mol\ CaCO_3}} = 1.4$ Tums tablets.

Exercise 5.3.3

Assume that as a result of overeating, a person's stomach contains 300 mL of 0.25 M HCl. How many Rolaids tablets must be consumed to neutralize 95% of the acid, if each tablet contains 400 mg of $NaAl(OH)_2CO_3$? The neutralization reaction can be written as follows:

$$NaAl(OH)_2CO_3(s) + 4HCl(aq) \rightarrow AlCl_3(aq) + NaCl(aq) + CO_2(g) + 3H_2O(l)$$

Answer: 6.4 tablets

The pH Scale

One of the key factors affecting reactions that occur in dilute solutions of acids and bases is the concentration of H^+ and OH^- ions. The pH scale provides a convenient way of expressing the hydrogen ion (H^+) concentration of a solution and enables us to describe acidity or basicity in quantitative terms.

Pure liquid water contains extremely low, but measurable concentrations of H_3O^+(aq) and OH^-(aq) ions produced via an *autoionization reaction*, in which water acts simultaneously as an acid and as a base:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{5.3.24}$$

The concentration of hydrogen ions in pure water is only 1.0×10^{-7} M at 25°C. Because the autoionization reaction produces both a proton and a hydroxide ion, the OH^- concentration in pure water is also 1.0×10^{-7} M. Pure water is a neutral solution in which the total positive charge from all the cations is matched by an identical total negative charge from all the anions. At room temperature this is $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M.

The pH scale describes the hydrogen ion concentration of a solution in a way that avoids the use of exponential notation. The negative base-10 logarithm of the hydrogen ion concentration: pH is often defined as the negative base-10 logarithm of the hydrogen ion concentration; pH is **actually** defined as the negative base-10 logarithm of hydrogen ion *activity*. As you will learn in a more advanced course, the activity of a substance in solution is related to its concentration. For dilute solutions such as those we are discussing, the activity and the concentration are approximately the same.

$$pH = -log[H^+] \tag{5.3.25}$$

Conversely,

$$[H^+] = 10^{-pH} \tag{5.3.26}$$

(If you are not familiar with logarithms or using a calculator to obtain logarithms and antilogarithms)

Because the hydrogen ion concentration is 1.0×10^{-7} M in pure water at 25°C, the pH of pure liquid water (and, by extension, of any neutral solution) is

$$pH = -\log[1.0 \times 10^{-7}] = 7.00 \tag{5.3.27}$$

Adding an acid to pure water increases the hydrogen ion concentration and decreases the hydroxide ion concentration because a neutralization reaction occurs, such as that shown in Equation 5.3.15. Because the negative exponent of $[H^+]$ becomes smaller as $[H^+]$ increases, the pH *decreases* with increasing $[H^+]$. For example, a 1.0 M solution of a strong monoprotic acid such as HCl or HNO_3 has a pH of 0.00:

$$pH = -\log[1.0] = 0.00 \tag{5.3.28}$$

Note

pH decreases with increasing $[H^+]$.

Conversely, adding a base to pure water increases the hydroxide ion concentration and decreases the hydrogen ion concentration. Because the autoionization reaction of water does not go to completion, neither does the neutralization reaction. Even a strongly basic solution contains a detectable amount of H^+ ions. For example, a 1.0 M OH^- solution has $[H^+] = 1.0 \times 10^{-14}$ M. The pH of a 1.0 M NaOH solution is therefore

$$pH = -log[1.0 \times 10^{-14}] = 14.00 \tag{5.3.29}$$

For practical purposes, the pH scale runs from pH = 0 (corresponding to 1 M H^+) to pH 14 (corresponding to 1 M OH^-), although pH values less than 0 or greater than 14 are possible.

We can summarize the relationships between acidity, basicity, and pH as follows:

- If pH = 7.0, the solution is neutral.
- If pH < 7.0, the solution is acidic.
- If pH > 7.0, the solution is basic.

Keep in mind that the pH scale is logarithmic, so a change of 1.0 in the pH of a solution corresponds to a *tenfold* change in the hydrogen ion concentration. The foods and consumer products we encounter daily represent a wide range of pH values, as shown in Figure 5.3.2.

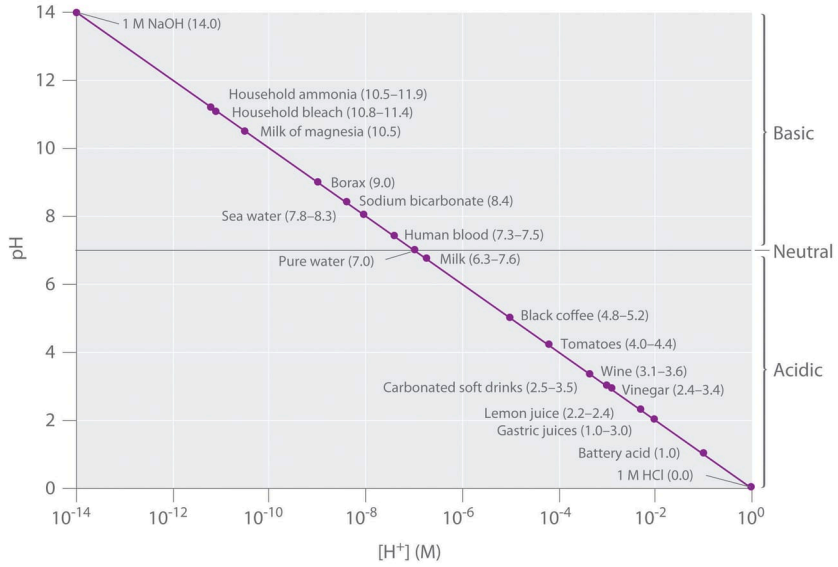


Figure 5.3.2 A Plot of pH versus [H^+] for Some Common Aqueous Solutions. Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.

Example 5.3.4

a. What is the pH of a 2.1×10^{-2} M aqueous solution of $HClO_4$?
b. The pH of a vinegar sample is 3.80. What is its hydrogen ion concentration?

Given: molarity of acid or pH

Asked for: pH or [H^+]

Strategy:

Using the balanced chemical equation for the acid dissociation reaction and Equation 5.3.25 or 5.3.24, determine [H^+] and convert it to pH or vice versa.

Solution:

a. $HClO_4$ (perchloric acid) is a strong acid, so it dissociates completely into H^+ ions and ClO_4^- ions:

$$HClO_4(l) \rightarrow H^+(aq) + ClO_4^-(aq)$$

The H^+ ion concentration is therefore the same as the perchloric acid concentration. The pH of the perchloric acid solution is thus

$$pH = -log[H^+] = -log(2.1 \times 10^{-2}) = 1.68$$

The result makes sense: the H^+ ion concentration is between 10^{-1} M and 10^{-2} M, so the pH must be between 1 and 2.

Note: The assumption that [H^+] is the same as the concentration of the acid is valid for *only* strong acids. Because weak acids do *not* dissociate completely in aqueous solution, a more complex procedure is needed to calculate the pH of their solutions.

b. We are given the pH and asked to calculate the hydrogen ion concentration. From Equation 5.3.24,

$$10^{-pH} = [H^+]$$

Thus $[H^+] = 10^{-3.80} = 1.6 \times 10^{-4}\ M$.

Exercise 5.3.4

a. What is the pH of a 3.0 × 10^{-5} M aqueous solution of HNO_3?
b. What is the hydrogen ion concentration of turnip juice, which has a pH of 5.41?

Answer

a. $pH = 4.52$
b. $[H^+] = 3.9 \times 10^{-6}\ M$

Tools have been developed that make the measurement of pH simple and convenient (Figures 5.3.3 and 5.3.4). For example, pH paper consists of strips of paper impregnated with one or more acid–base indicators, which are intensely colored organic molecules whose colors change dramatically depending on the pH of the solution. Placing a drop of a solution on a strip of pH paper and comparing its color with standards give the solution's approximate pH. A more accurate tool, the pH meter, uses a glass electrode, a device whose voltage depends on the H^+ ion concentration (Figure 5.3.4).



Figure 5.3.3: These pH strips can measure pH in a series of ranges by putting sample on a strip and comparing its color change with colors on the box that correspond to a certain pH. The strip on the left measures pH 0-7 and shows results of a strong acid sample; the center strip is pH range 5-10 and shows results of a 6.97 buffer solution sample; the strip on the right measures a broad range (pH 1-14) and shows results of a 10% bleach water solution sample. This image can be enlarged by clicking on it. Photo by Monica Bruckner (courtesy of the Science Education Resource Center (SERC) at Carleton College).



Figure 5.3.4: These three meters and probes can measure pH (left) and electrical conductivity (center and right). The image can be enlarged if you click on it. Photo by Monica Bruckner (courtesy of the Science Education Resource Center (SERC) at Carleton College).

YouTube Video

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View this YouTube Video online

Introduction to pH: https://youtu.be/pQOa3bb5YEE

Summary

An acidic solution and a basic solution react together in a neutralization reaction that also forms a salt. Acid–base reactions require both an acid and a base. In Brønsted–Lowry terms, an **acid** is a substance that can donate a proton (H^+), and a **base** is a substance that can accept a proton. All acid–base reactions contain two acid–base pairs: the reactants and the products. Acids can donate one proton (**monoprotic acids**), two protons (**diprotic acids**), or three protons (**triprotic acids**). Compounds that are capable of donating more than one proton are generally called **polyprotic acids**. Acids also differ in their tendency to donate a proton, a measure of their acid strength. **Strong acids** react completely with water to produce $H_3O^+(aq)$ (the **hydronium ion**), whereas **weak acids** dissociate only partially in water. Conversely, **strong bases** react completely with water to produce the hydroxide ion, whereas **weak bases** react only partially with water to form hydroxide ions. The reaction of a strong acid with a strong base is a **neutralization reaction**, which produces water plus a **salt**.

The acidity or basicity of an aqueous solution is described quantitatively using the **pH scale**. The **pH** of a solution is the negative logarithm of the H^+ ion concentration and typically ranges from 0 for strongly acidic solutions to 14 for strongly basic ones. Because of the *autoionization reaction* of water, which produces small amounts of hydronium ions and hydroxide ions, a **neutral solution** of water contains 1×10^{-7} M H^+ ions and has a pH of 7.0. An **indicator** is an intensely colored organic substance whose color is pH dependent; it is used to determine the pH of a solution.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

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5.4: Oxidation-Reduction: Some General Principles

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, coherent, 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.

Note

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). The reaction is as follows:

$$Cu_2O(s) + H_2(g) \rightarrow 2Cu(s) + H_2O(g) \tag{5.4.1}$$

Oxidation and reduction reactions are now defined as reactions that exhibit a change in the oxidation states of one or more elements in the reactants, 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

$$4Al(s) + 3O_2 \rightarrow 2Al_2O_3(s) \tag{5.4.2}$$

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 superscript 0 emphasizes the oxidation state of the elements):

$$4Al^0 + 3O_2^0 \rightarrow 4Al^{3+} + 6O^{2-} \tag{5.4.3}$$

Equation 5.4.1 and Equation 5.4.2 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 5.4.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$electrons\,lost = 4\,Al\,atoms \times \frac{3\,e^-\,lost}{Al\,atom} = 12\,e^-\,lost \tag{5.4.4}$$

Label '5.4.4a' multiply defined

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 oxygen in air, is illustrated in Figure 5.4.1.

Note

In all oxidation–reduction (redox) reactions, the number of electrons lost equals the number of electrons gained.

YouTube Video

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Redox Reactions: https://youtu.be/1v3yaaR_nHc

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. Previosuly, 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 5.4.1), magnesium oxide (MgO), and calcium chloride ($CaCl_2$). In covalent compounds, in contrast, atoms share electrons. Oxidation states in covalent compounds are somewhat arbitrary, but they are useful bookkeeping devices to help you understand and predict many reactions.

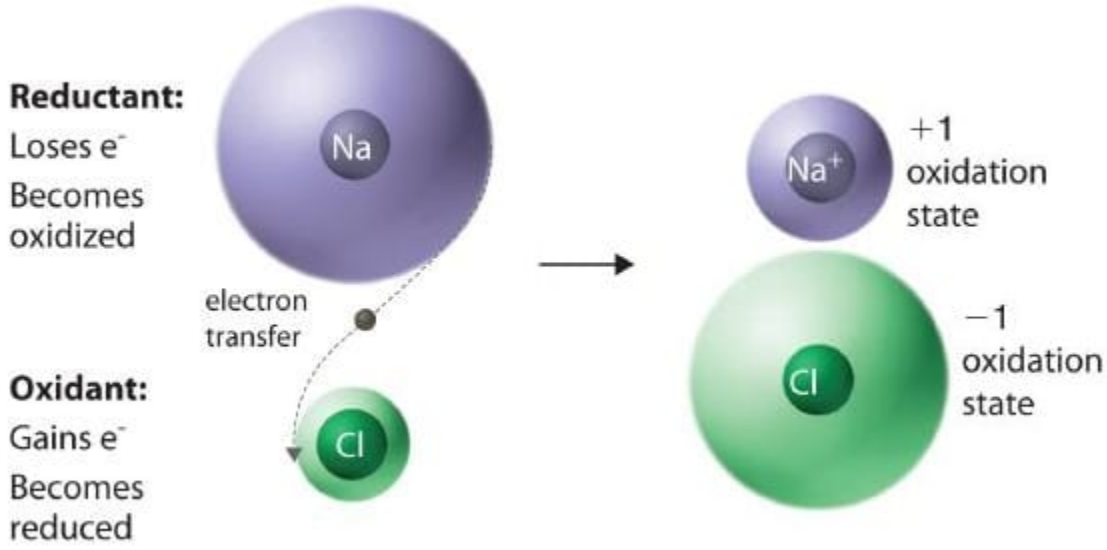


Figure 5.4.1: The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom. The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.

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 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 5.4.5 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:

$$\overset{+1}{Cu}_2\overset{}{O}_{-2}(s) + \overset{0}{H}_2(g) \rightarrow 2\overset{0}{Cu}(s) + \overset{+1}{H}_2\overset{}{O}_{-2}(g) \tag{5.4.5}$$

Assigning oxidation states allows us to see that there has been a net transfer of electrons from hydrogen (0 → +1) to copper (+1 → 0). So 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:

$$electrons\,lost = 2\,H\,atoms \times \frac{1\,e^-\,lost}{H\,atom} = 2\,e^-\,lost \tag{5.4.6}$$

$$electrons\,gained = 2\,Cu\,atoms \times \frac{1\,e^-\,gained}{Cu\,atom} = 2\,e^-\,gained \tag{5.4.7}$$

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 5.4.1

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:

$$[(6\text{ F atoms})(-1)] + [(1\text{ S atom})(+6)] = 0$$

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:

$$[(4\text{ H atoms})(+1)] + [(1\text{ O atom})(-2)] + [(1\text{ C atom})(-2)] = 0$$

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:

$$[(4\text{ H atoms})(+1)] + [(1\text{ N atom})(-3)] = +1, \text{ the charge on the } NH_4^+ \text{ ion}$$

For SO42–, oxygen has an oxidation state of –2 (rule 5), so sulfur must have an oxidation state of +6:

$$[(4\text{ O atoms})(-2)] + [(1\text{ S atom})(+6)] = -2, \text{ the charge on the sulfate ion}$$

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:

$$[(4\text{ O atoms})(-2)] + [(3\text{ Fe atoms})\left(+\tfrac{8}{3}\right)] = 0$$

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

$$[(4\text{ H atoms})(+1)] + [(2\text{ O atoms})(-2)] = 0$$

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

$$[(2\text{ O atoms})(-2)] + [(1\text{ H atom})(+1)] = -3$$

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

$$\overset{+1}{\underset{-3}{C}}\overset{}{H_3}\overset{+3}{C}\overset{}{O_2}\overset{+1}{\underset{-2}{H}} \tag{5.4.8}$$

Thus the sum of the oxidation states of the two carbon atoms is indeed zero.

Exercise 5.4.1

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. Ba, +2; F, −1
b. C, 0; H, +1; O, −2
c. K, +1; Cr, +6; O, −2
d. Cs, +1; O, −½
e. C, −3; H, +1; C, −1; H, +1; O, −2; H, +1

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 5.4.1). 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:

Label '5.4.5' multiply defined

In subsequent steps, $FeCl_2$ undergoes oxidation to form a reddish-brown precipitate of $Fe(OH)_3$.



Figure 5.4.2: 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

$$metal + acid \rightarrow salt + hydrogen \tag{5.4.9}$$

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:

$$Pb(s) + 2H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g) \tag{5.4.10}$$

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 5.4.8) and the reduction of silver salts by copper (Equation 5.4.9 and Figure 5.4.2):

$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s) \tag{5.4.11}$$

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s) \tag{5.4.12}$$

The reaction in Equation 5.4.8 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

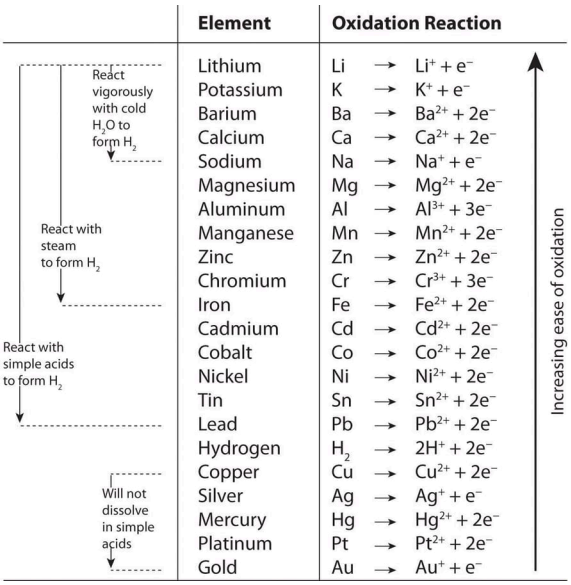
By observing what happens when samples of various metals are placed in contact with solutions of other metals, chemists have arranged the metals according to the relative ease or difficulty with which they can be oxidized in a single-displacement reaction. For example, metallic zinc reacts with iron salts, and metallic copper reacts with silver salts. Experimentally, it is found that zinc reacts with both copper salts and silver salts, producing 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:

$$Zn(s) + Mg^{2+}(aq) \not\rightarrow Zn^{2+}(aq) + Mg(s) \tag{5.4.13}$$

$$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s) \tag{5.4.14}$$

Magnesium has a greater tendency to be oxidized than zinc does.

Pairwise reactions of this sort are the basis of the activity series (Figure $5.4.4$), 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).



Element	Oxidation Reaction
Lithium	$Li \rightarrow Li^+ + e^-$
Potassium	$K \rightarrow K^+ + e^-$
Barium	$Ba \rightarrow Ba^{2+} + 2e^-$
Calcium	$Ca \rightarrow Ca^{2+} + 2e^-$
Sodium	$Na \rightarrow Na^+ + e^-$
Magnesium	$Mg \rightarrow Mg^{2+} + 2e^-$
Aluminum	$Al \rightarrow Al^{3+} + 3e^-$
Manganese	$Mn \rightarrow Mn^{2+} + 2e^-$
Zinc	$Zn \rightarrow Zn^{2+} + 2e^-$
Chromium	$Cr \rightarrow Cr^{3+} + 3e^-$
Iron	$Fe \rightarrow Fe^{2+} + 2e^-$
Cadmium	$Cd \rightarrow Cd^{2+} + 2e^-$
Cobalt	$Co \rightarrow Co^{2+} + 2e^-$
Nickel	$Ni \rightarrow Ni^{2+} + 2e^-$
Tin	$Sn \rightarrow Sn^{2+} + 2e^-$
Lead	$Pb \rightarrow Pb^{2+} + 2e^-$
Hydrogen	$H_2 \rightarrow 2H^+ + 2e^-$
Copper	$Cu \rightarrow Cu^{2+} + 2e^-$
Silver	$Ag \rightarrow Ag^+ + e^-$
Mercury	$Hg \rightarrow Hg^{2+} + 2e^-$
Platinum	$Pt \rightarrow Pt^{2+} + 2e^-$
Gold	$Au \rightarrow Au^+ + e^-$

Figure 5.4.4: 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 5.4.4, 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 5.4.2 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions.

Example 5.4.2

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

1. A strip of aluminum foil is placed in an aqueous solution of silver nitrate.
2. A few drops of liquid mercury are added to an aqueous solution of lead(II) acetate.
3. 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 .5.4.4 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:

$$Al(s) + 3Ag^+(aq) \rightarrow Al^{3+}(aq) + 3Ag(s) \tag{5.4.15}$$

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:

$$Pb(s) + 2H^+(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + H_2(g) \tag{5.4.16}$$

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 5.4.2

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

1. A strip of chromium metal is placed in an aqueous solution of aluminum chloride.
2. A strip of zinc is placed in an aqueous solution of chromium(III) nitrate.
3. A piece of aluminum foil is dropped into a glass that contains vinegar (the active ingredient is acetic acid).

Answer

1. $no\ reaction$
2. $3Zn(s) + 2Cr^{3+}(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr(s)$
3. $2Al(s) + 6CH_3CO_2H(aq) \rightarrow 2Al^{3+}(aq) + 6CH_3CO_2^-(aq) + 3H_2(g)$

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 5.4.1), in which the overall reaction is separated into an oxidation equation and a reduction equation. **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 5.4.4), 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.

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5.5: Balancing Oxidation-Reduction Equations

The Learning Objectives of this Module are:

1. To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions already. 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 state*s, and a second is referred to as the *half-reaction* method. We show you how to balance redox equations using oxidation states in this section; the half-reaction method is discussed in the second semester

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 8.8.1 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 in Section 7.5:

$$\underset{}{\overset{+2}{Cr^{2+}}\,(aq)} + \underset{}{\overset{\begin{matrix}+4\\-2\end{matrix}}{MnO_2}\,(aq)} + \underset{}{\overset{+1}{H^+}\,(aq)} \rightarrow \underset{}{\overset{+3}{Cr^{3+}}\,(aq)} + \underset{}{\overset{+2}{Mn^{2+}}\,(aq)} + \underset{}{\overset{\begin{matrix}+1\\-2\end{matrix}}{H_2O}\,(l)}$$

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:

$$Cr^{2+} + Mn^{4+} \rightarrow Cr^{3+} + Mn^{2+}$$

The oxidation can be written as

$$Cr^{2+} \rightarrow Cr^{3+} + e^-$$

and the reduction as

$$Mn^{4+} + 2e^- \rightarrow Mn^{2+}$$

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 by 2 to give

$$2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^-$$

Note the Patterns
In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction:

$$2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^-$$

$$Mn^{4+} + 2e^- \rightarrow Mn^{2+}$$

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:

$$2Cr^{2+}\,(aq) \rightarrow 2Cr^{3+}\,(aq) + \cancel{2e^-}$$

$$2Cr^{2+}\,(aq) + \cancel{2e^-} \rightarrow Mn^{2+}\,(aq)$$

$$2Cr^{2+}\,(aq) + 2Cr^{2+}\,(aq) \rightarrow 2Cr^{3+}\,(aq) + Mn^{2+}\,(aq)$$

Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of the equation (+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 the equation gives

$$2Cr^{2+}(aq) + MnO_2(s) + 4H^+(aq) \rightarrow 2Cr^{3+}(aq) + Mn^{2+}(aq)$$

Although the charges are now balanced, 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:

$$2Cr^{2+}(aq) + MnO_2(s) + 4H^+(aq) \rightarrow 2Cr^{3+}(aq) + Mn^{2+}(aq) + 2H_2O(l)$$

Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized in Table 8.8.1 and illustrated in Example 17.

Table 8.8.1 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 (see Section 3.5) 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 17

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:

$$H_3AsO_4(aq) + Zn(s) \rightarrow AsH_3(g) + Zn^{2+}(aq)$$

Given: reactants and products in acidic solution

Asked for: balanced chemical equation using oxidation states

Strategy:

Follow the procedure given in Table 8.8.1 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 using the procedure described in Section 3.5 and determine which atoms change oxidation state.** The oxidation state of arsenic in arsenic acid is +6, 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:

$$[\mathrm{H_3\overset{+5}{As}O_4(aq) + \overset{0}{Zn}(s) \rightarrow \underset{-3}{As}H_3(g) + \overset{+2}{Zn^{2+}}(aq)}]$$

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:

$$Reduction\text{:}\ \underset{-3}{As^{3-}} + 8e^- \rightarrow As^{5+}$$

Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom:

$$Oxidation\text{:}\ Zn \rightarrow Zn^{2+} + 2e^-$$

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

$$Reduction\ (\times 1)\text{:}\ As^{5+} + 8e^- \rightarrow As^{3-} \tag{5.5.1}$$
$$Oxidation\ (\times 4)\text{:}\ 4Zn^0 \rightarrow 4Zn^{2+} + 8e^- \tag{5.5.2}$$

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

$$Reduction\text{:}\ H_3AsO_4(aq) + 8e^- \rightarrow AsH_3(g) \tag{5.5.3}$$
$$Oxidation\text{:}\ 4Zn(s) \rightarrow 4Zn^{2+}(aq) + 8e^- \tag{5.5.4}$$

6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is

$$H_3AsO_4(aq) + 4Zn(s) + \cancel{8e^-} \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + \cancel{8e^-}$$

which then yields

$$H_3AsO_4(aq) + 4Zn(s) \rightarrow AsH_3(g) + 4Zn^{2+}(aq)$$

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:

$$H_3AsO_4(aq) + 4Zn(s) + 8H^+(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq)$$

8. *Balance the oxygen atoms by adding H_2O molecules to one side of the equation.* There are 4 O atoms on the left side of the

equation. Adding 4 H_2O molecules to the right side balances the O atoms:

$$H_3AsO_4(aq) + 4Zn(s) + 8H^+(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + 4H_2O(l)$$

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:

$$Atoms: 1As + 4Zn + 4O + 11H = 1As + 4Zn + 4O + 11H \quad (5.5.5)$$
$$Total\ charge: 8(+1) = 4(+2) = +8 \quad (5.5.6)$$

The balanced chemical equation for the reaction is therefore:

$$H_3AsO_4(aq) + 4Zn(s) + 8H^+(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + 4H_2O(l)$$

Exercise

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:

$$CuS(s) + H^+(aq) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO(g) + SO_4^{2-}(aq)$$

Answer: $3CuS(s) + 8H^+(aq) + 8NO_3^-(aq) \rightarrow 3Cu^{2+}(aq) + 8NO(g) + 3SO_4^{2-}(aq) + 4H_2O(l)$

Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example 18.

Example 18

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:

$$Al(s) + H_2O(aq) \rightarrow [Al(OH)_4]^-(aq) + H_2(g)$$

Balance this equation using oxidation states.

Given: reactants and products in a basic solution

Asked for: balanced chemical equation

Strategy:

Follow the procedure given in Table 8.8.1 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 17 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 $[Al(OH)_4]^-$. The oxidation state of hydrogen changes from +1 in H_2O to 0 in 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. $Reduction: Al^0 \rightarrow Al^{3+} + 3e^-$ (5.5.7)
   $Oxidation: H^+ + e^- \rightarrow H^0\ (in\ H_2)$ (5.5.8)

4. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:

   $Reduction: 3H^+ + 3e^- \rightarrow 3H^0\ (in\ H_2)$ (5.5.9)
   $Oxidation: Al^0 \rightarrow Al^{3+} + 3e^-$ (5.5.10)

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 H_2O contains two protons, in this case, $3H^+$ corresponds to $3/2H_2O$. Similarly, each molecule of hydrogen gas contains two H atoms, so 3H corresponds to $3/2H_2$.

   $Reduction: \frac{3}{2}H_2O + 3e^- \rightarrow \frac{3}{2}H_2$ (5.5.11)
   $Oxidation: Al \rightarrow [Al(OH)_4]^- + 3e^-$ (5.5.12)

6. Adding the equations and canceling the electrons gives

$$Al + \frac{3}{2}H_2O + \cancel{3e^-} \rightarrow [Al(OH)_4]^- + \frac{3}{2}H_2 + \cancel{3e^-}$$
$$Al + \frac{3}{2}H_2O \rightarrow [Al(OH)_4]^- + \frac{3}{2}H_2$$

   To remove the fractional coefficients, multiply both sides of the equation by 2:

$$2Al + 3H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$$

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 OH^- ions to the left side:

$$2Al + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$$

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:

$$2Al + 2OH^- + 6H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$$

9. Be sure the equation is balanced:

   $Atoms: 2Al + 8O + 14H = 2Al + 8O + 14H$ (5.5.13)
   $Total\ charge: (2)(0) + (2)(-1) + (6)(0) = (2)(-1) + (3)(0)$ (5.5.14)
   $-2 = -2$

10. The balanced chemical equation is therefore

$$2Al(s) + 2OH^-(aq) + 6H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$$

    Thus 3 mol of H_2 gas are produced for every 2 mol of Al.

Exercise

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: $2MnO_4^-(aq) + 3NO_2^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + 3NO_3^-(aq) + 2OH^-(aq)$

As suggested in Example 17 and Example 18, 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.

Note the Pattern
Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.

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.

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 8.8.1). 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:

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$$

In subsequent steps, $FeCl_2$ undergoes oxidation to form a reddish-brown precipitate of $Fe(OH)_3$.



Figure 8.8.1 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

$$metal + acid \rightarrow salt + hydrogen$$

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:

$$Pb(s) + 2H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$$

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 8.8.13) and the reduction of silver salts by copper (Equation 8.8.14 and Figure 8.8.2):

$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$$

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

The reaction in Equation 8.8.13 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.



Figure 8.8.2 The Single-Displacement Reaction of Metallic Copper with a Solution of Silver Nitrate. *When a copper coil is placed in a solution of silver nitrate, silver ions are reduced to metallic silver on the copper surface, and some of the copper metal dissolves. Note the formation of a metallic silver precipitate on the copper coil and a blue color in the surrounding solution due to the presence of aqueous* Cu^{2+} *ions.* Figure used with permission of Wikipedia

Summary

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 8.8.1), in which the overall reaction is separated into an oxidation equation and a reduction equation.

Key Takeaway

- Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation.

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.

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. $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$

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5.6: Oxidizing and Reducing Agents

Compounds that are capable of accepting electrons, such as O_2 or F_2, are called oxidants (or oxidizing agents) because they can oxidize other compounds. In the process of accepting electrons, an oxidant is reduced. Compounds that are capable of donating electrons, such as sodium metal or cyclohexane (C_6H_{12}), are called reductants (or reducing agents) because they can cause the reduction of another compound. In the process of donating electrons, a reductant is oxidized. These relationships are summarized in Equation 3.30:

$$\text{oxidant + reductant} \rightarrow \text{oxidation–reduction}$$

$$\underset{gains\ e\ (is\ reduced)}{O_2(g)} + \underset{loses\ e\ (is\ oxidized)}{4Na(s)} \rightarrow \underset{redox\ reaction}{2\ Na_2O(s)} \tag{3.30}$$

Some oxidants have a greater ability than others to remove electrons from other compounds. Oxidants can range from very powerful, capable of oxidizing most compounds with which they come in contact, to rather weak. Both F_2 and Cl_2 are powerful oxidants: for example, F_2 will oxidize H_2O in a vigorous, potentially explosive reaction. In contrast, S_8 is a rather weak oxidant, and O_2 falls somewhere in between. Conversely, reductants vary in their tendency to donate electrons to other compounds. Reductants can also range from very powerful, capable of giving up electrons to almost anything, to weak. The alkali metals are powerful reductants, so they must be kept away from atmospheric oxygen to avoid a potentially hazardous redox reaction.

A combustion reaction, first introduced in Section 3.2 "Determining Empirical and Molecular Formulas", is an oxidation–reduction reaction in which the oxidant is O_2. One example of a combustion reaction is the burning of a candle, shown in Figure 3.9 "An Example of a Combustion Reaction". Consider, for example, the combustion of cyclohexane, a typical hydrocarbon, in excess oxygen. The balanced chemical equation for the reaction, with the oxidation state shown for each atom, is as follows:

$$\overset{+1}{\underset{-2}{C_6H_{12}}} + 9\overset{0}{O_2} \rightarrow 6\overset{+4}{\underset{-2}{CO_2}} + 6\overset{+1}{\underset{-2}{H_2O}} \tag{3.31}$$

If we compare the oxidation state of each element in the products and the reactants, we see that hydrogen is the only element whose oxidation state does not change; it remains +1. Carbon, however, has an oxidation state of –2 in cyclohexane and +4 in CO_2; that is, each carbon atom changes its oxidation state by six electrons during the reaction. Oxygen has an oxidation state of 0 in the reactants, but it gains electrons to have an oxidation state of –2 in CO_2 and H_2O. Because carbon has been oxidized, cyclohexane is the reductant; because oxygen has been reduced, it is the oxidant. All combustion reactions are therefore oxidation–reduction reactions.

We described the defining characteristics of oxidation–reduction, or redox, reactions in Chapter 7. 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. We show you how to balance redox equations using oxidation states in this section; the half-reaction method is discussed in the second semester

Note the Pattern
Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.

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.

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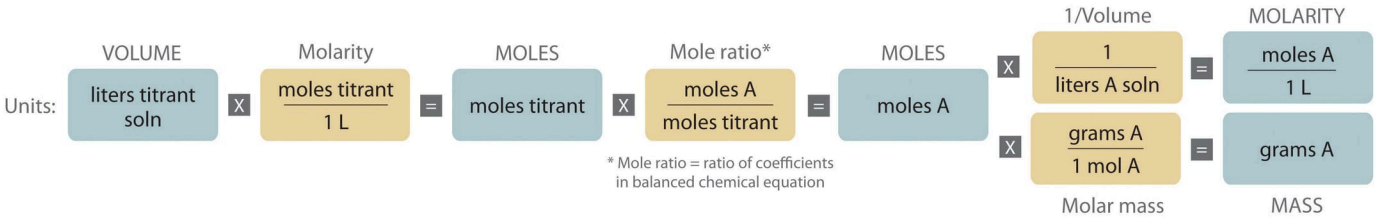
5.7: Stoichiometry of Reactions in Aqueous Solutions: Titrations

The Learning Objective of this Module is 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 (A methodology that combines chemical reactions and stoichiometric calculations to determine the amounts or concentrations of substances present in a sample). 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 titrationAn experimental procedure in which a carefully measured volume of a solution of known concentration is added to a measured volume of a solution containing a compound whose concentration is to be determined., a carefully measured volume of a solution of known concentration, called the titrantThe solution of known concentration that is reacted with a compound in a solution of unknown concentration in a titration., 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 (The point in a titration where a stoichiometric amount (i.e., the amount required to react completely with the unknown) of the titrant has been added) 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:



Example 20

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:

$$\begin{pmatrix} MnO_4^-\,(aq) + HO_2CCO_2H\,(aq) & \rightarrow Mn^{2+}\,(aq) & +CO_2\,(g) + H_2O\,(l) \\ purple & colorless & \end{pmatrix}$$

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. The following video (chemistry Nakajima) demonstrates the reaction

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Figure 8.9.1

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 (Figure 8.3.1). 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 permaganage added equals the number of moles of oxalate in the solution, thus determining how many moles of oxalate we started with

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Figure 8.9.2 Titration of oxalate using a known permaganate solution *As permanganate is added to the oxalate solution the purple color appears and then disappears as the permanganate is consumed. As more permanganate is added, eventually all the oxalate is oxidized, and a faint purple color from the presence of excess permanganate appears, marking the endpoint.*

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

$$2MnO_4^-(aq) + 5HO_2CCO_2H(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l) \tag{5.7.1}$$

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^-

$$15.4 \cancel{mL}\left(\frac{1 \cancel{L}}{1000 \cancel{mL}}\right)\left(\frac{0.0247\ mol\ MnO_4^-}{1 \cancel{L}}\right) = 3.80 \times 10^4\ mol\ MnO_4^- \tag{5.7.2}$$

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

$$moles\ HO_2CCO_2H = 3.80 \times 10^{-4}\ \cancel{mol\ MnO_4^-}\left(\frac{5\ mol\ HO_2CCO_2H}{2\ \cancel{mol\ MnO_4^-}}\right) \tag{5.7.3}$$

$$= 9.50 \times 10^{-4}\ mol\ HO_2CCO_2H \tag{5.7.4}$$

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:

$$Ca(O_2CCO_2)(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + HO_2CCO_2H(aq) \tag{5.7.5}$$

The mass of calcium oxalate originally present was thus

$$mass\ of\ CaC_2O_4 = 9.50 \times 10^{-4}\ \cancel{mol\ HO_2CCO_2H}\left(\frac{1\ \cancel{mol\ CaC_2O_4}}{1\ \cancel{mol\ HO_2CCO_2H}}\right)\left(\frac{128.10\ g\ CaC_2O_4}{1\ \cancel{mol\ CaC_2O_4}}\right) \tag{5.7.6}$$

$$= 0.122\ g\ CaC_2O_4 \tag{5.7.7}$$

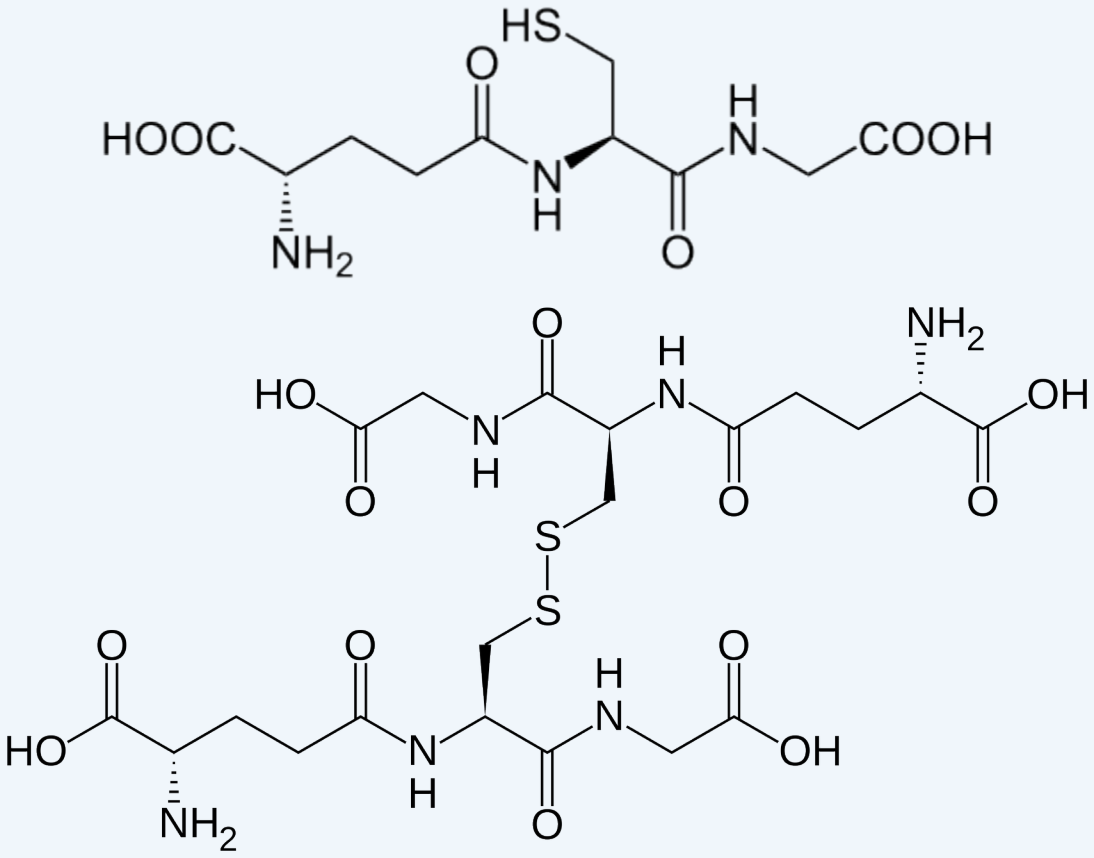
The original sample contained 0.122 g of calcium oxalate per 10.0 g of rhubarb. The percentage of calcium oxalate by mass was thus

$$\%CaC_2O_4 = \frac{0.122\ g}{10.0\ g} \times 100 = 1.22\% \tag{5.7.8}$$

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 20: 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:

$$2GSH(aq) + I_2(aq) \rightarrow GSSG(aq) + 2HI(aq) \tag{5.7.9}$$

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.

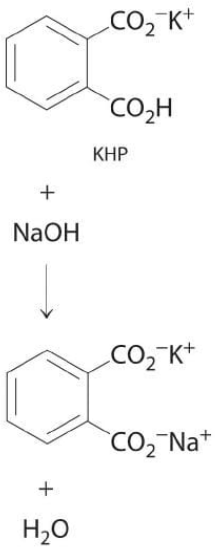
Adding small volumes of a 0.0031 M aqueous solution of I_2 to 194 mL of a solution that contains glutathione and a trace of soluble starch initially causes no change. After 16.3 mL of iodine solution have been added, however, a permanent pale blue color appears because of the formation of the starch-iodine complex. What is the concentration of glutathione in the original solution?

Answer: 5.2×10^{-4} M

Standard Solutions

In Example 20, 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 solutionA solution whose concentration is precisely known., 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.



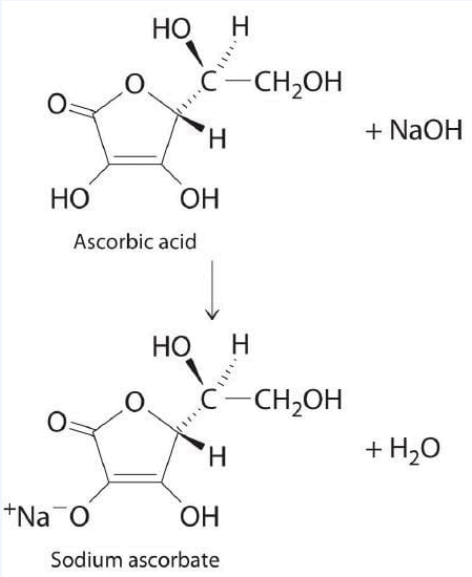
The reaction of KHP with NaOH. As with all acid-base reactions, a salt is formed.

Acid–Base Titrations

Because most common acids and bases are not intensely colored, a small amount of an acid–base **indicator** is usually added to detect the equivalence point in an acid–base titration. The point in the titration at which an indicator changes color is called the endpoint (the point in a titration at which an indicator changes color). The procedure is illustrated in Example 21.

Example 21: Vitamin C

The structure of vitamin C (ascorbic acid, a monoprotic acid) is as follows:



Ascorbic acid. The upper figure shows the three-dimensional representation of ascorbic acid. Hatched lines indicate bonds that are behind the plane of the paper, and wedged lines indicate bonds that are out of the plane of the paper.

An absence of vitamin C in the diet leads to the disease known as scurvy, a breakdown of connective tissue throughout the body and of dentin in the teeth. Because fresh fruits and vegetables rich in vitamin C are readily available in developed countries today, scurvy is not a major problem. In the days of slow voyages in wooden ships, however, scurvy was common. Ferdinand Magellan, the first person to sail around the world, lost more than 90% of his crew, many to scurvy. Although a diet rich in fruits and vegetables contains more than enough vitamin C to prevent scurvy, many people take supplemental doses of vitamin C, hoping that the extra amounts will help prevent colds and other illness.

Suppose a tablet advertised as containing 500 mg of vitamin C is dissolved in 100.0 mL of distilled water that contains a small amount of the acid–base indicator bromothymol blue, an indicator that is yellow in acid solution and blue in basic solution, to give a yellow solution. The addition of 53.5 mL of a 0.0520 M solution of NaOH results in a change to green at the endpoint, due to a mixture of the blue and yellow forms of the indicator (**Figure 8.9.3**). What is the actual mass of vitamin C in the tablet? (The molar mass of ascorbic acid is 176.13 g/mol.)

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Figure 8.9.3: Bromothymol Blue is used as an indicator. If placed in a acidic solution it will turn the solution yellow, and if placed in a basic solution it will turn the solution blue. The equivalence point is seen when the solution turns green. pH is important for a variety of reasons. For example if you are trying to discard an acidic solution, you could add bromothymol blue to the solution and then titrate in some base until the solution turned green. This indicates that it is neutral

Given: reactant, volume of sample solution, and volume and molarity of titrant

Asked for: mass of unknown

Strategy:

A Write the balanced chemical equation for the reaction and calculate the number of moles of base needed to neutralize the ascorbic acid.

B Using mole ratios, determine the amount of ascorbic acid consumed. Calculate the mass of vitamin C by multiplying the number of moles of ascorbic acid by its molar mass.

Solution:

A Because ascorbic acid acts as a monoprotic acid, we can write the balanced chemical equation for the reaction as

$$HAsc(aq) + OH^-(aq) \rightarrow Asc^-(aq) + H_2O(l) \tag{5.7.10}$$

where HAsc is ascorbic acid and Asc^- is ascorbate. The number of moles of OH^- ions needed to neutralize the ascorbic acid is

$$moles\ OH^- = 53.5\ \cancel{mL}\left(\frac{\cancel{1L}}{1000\ \cancel{mL}}\right)\left(\frac{0.0520\ mol\ OH^-}{\cancel{1L}}\right) = 2.78 \times 10^{-3}\ mol\ OH^- \tag{5.7.11}$$

B The mole ratio of the base added to the acid consumed is 1:1, so the number of moles of OH^- added equals the number of moles of ascorbic acid present in the tablet:

$$mass\ ascorbic\ acid = 2.78 \times 10^{-3}\ \cancel{mol\ HAsc}\left(\frac{176.13\ g\ HAsc}{1\ \cancel{mol\ HAsc}}\right) = 0.490\ g\ HAsc \tag{5.7.12}$$

Because 0.490 g equals 490 mg, the tablet contains about 2% less vitamin C than advertised.

Exercise 20: Vinegar

Vinegar is essentially a dilute solution of acetic acid in water. Vinegar is usually produced in a concentrated form and then diluted with water to give a final concentration of 4%–7% acetic acid; that is, a 4% m/v solution contains 4.00 g of acetic acid per 100 mL of solution. If a drop of bromothymol blue indicator is added to 50.0 mL of concentrated vinegar stock and 31.0 mL of 2.51 M NaOH are needed to turn the solution from yellow to green, what is the percentage of acetic acid in the vinegar stock? (Assume that the density of the vinegar solution is 1.00 g/mL.)

Answer: 9.35%

Summary

The concentration of a species in solution can be determined by **quantitative analysis**. One such method is a **titration**, in which a measured volume of a solution of one substance, the **titrant**, is added to a solution of another substance to determine

its concentration. The **equivalence point** in a titration is the point at which exactly enough reactant has been added for the reaction to go to completion. A **standard solution**, a solution whose concentration is known precisely, is used to determine the concentration of the titrant. Many titrations, especially those that involve acid–base reactions, rely on an indicator. The point at which a color change is observed is the **endpoint**, which is close to the equivalence point if the indicator is chosen properly.

Key Takeaway

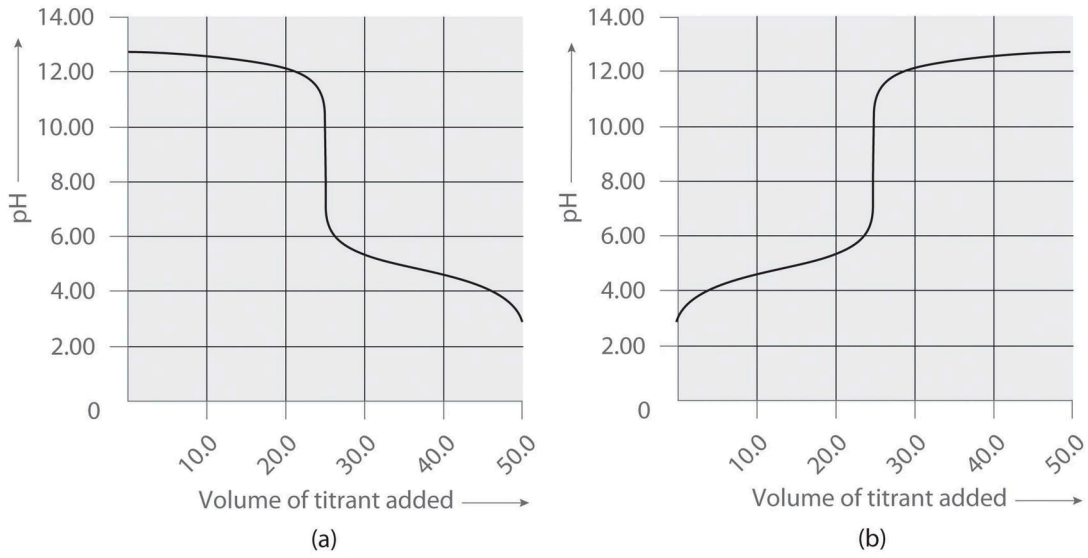
- Quantitative analysis of an unknown solution can be achieved using titration methods.

Conceptual Problems

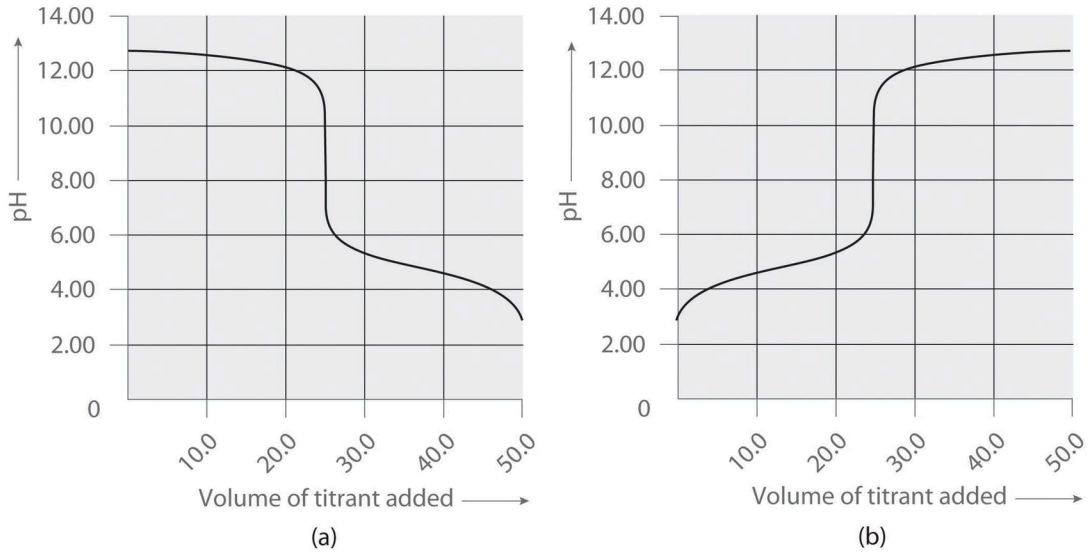
1. The titration procedure is an application of the use of limiting reactants. Explain why this is so.

2. Explain how to determine the concentration of a substance using a titration.

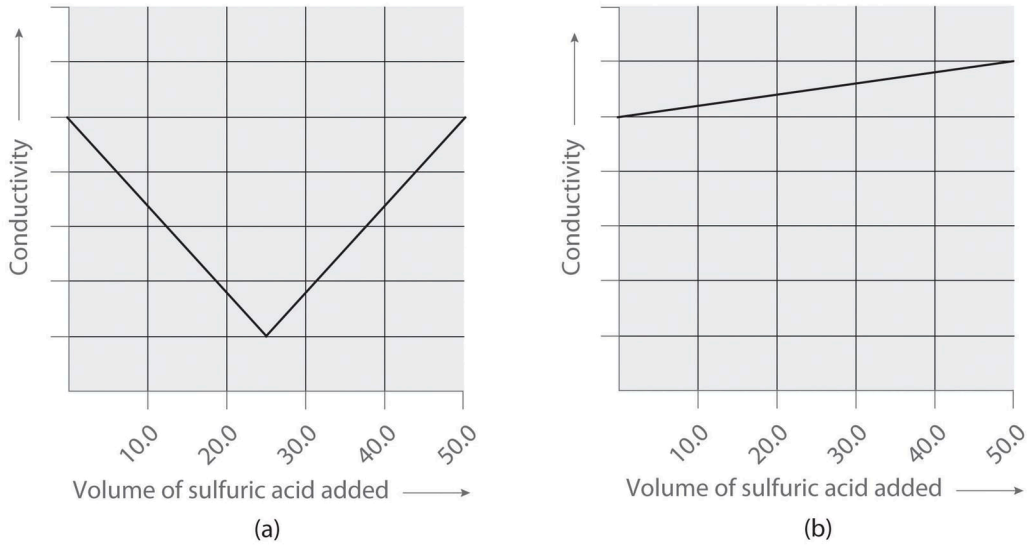
3. Following are two graphs that illustrate how the pH of a solution varies during a titration. One graph corresponds to the titration of 100 mL 0.10 M acetic acid with 0.10 M NaOH, and the other corresponds to the titration of 100 mL 0.10 M NaOH with 0.10 M acetic acid. Which graph corresponds to which 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.



Answers

1.
2.

3. 1. titration of NaOH with acetic acid
   2. titration of acetic acid with NaOH
4.
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?

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6: GASES

Petrucci: *General Chemistry*
Principles and Modern Applications

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6.1: Properties of Gases: Gas Pressure

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 6.1.1 compares the three states of matter and illustrates the differences at the molecular level.

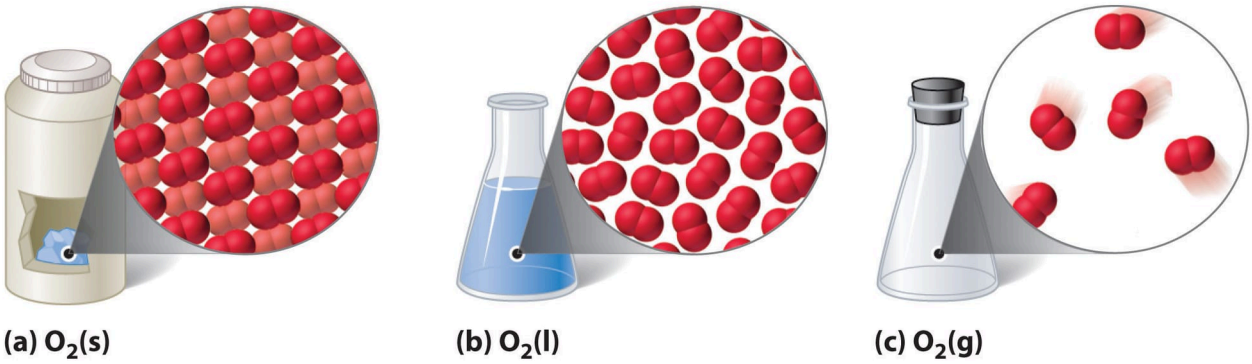


Figure 6.1.1: A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States: (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (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 6.1.1.

Table 6.1.1: Properties of Water at 1.0 atm

Temperature	State	Density (g/cm^3)
≤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 6.1.2 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.

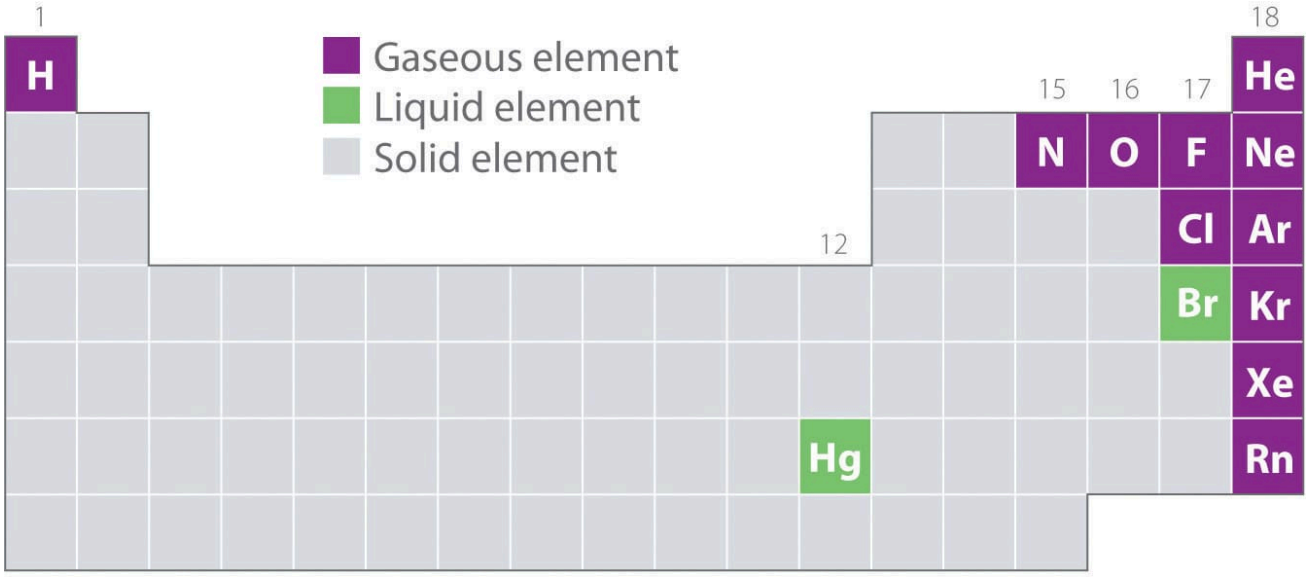


Figure 6.1.2: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

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.

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Defining Gas Pressure: https://youtu.be/_CRn3cFs2CI

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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6.2: The Simple 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.

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 $6.2.1$. 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 $6.2.2$). 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:

$$PV = \text{constant} \tag{6.2.1}$$

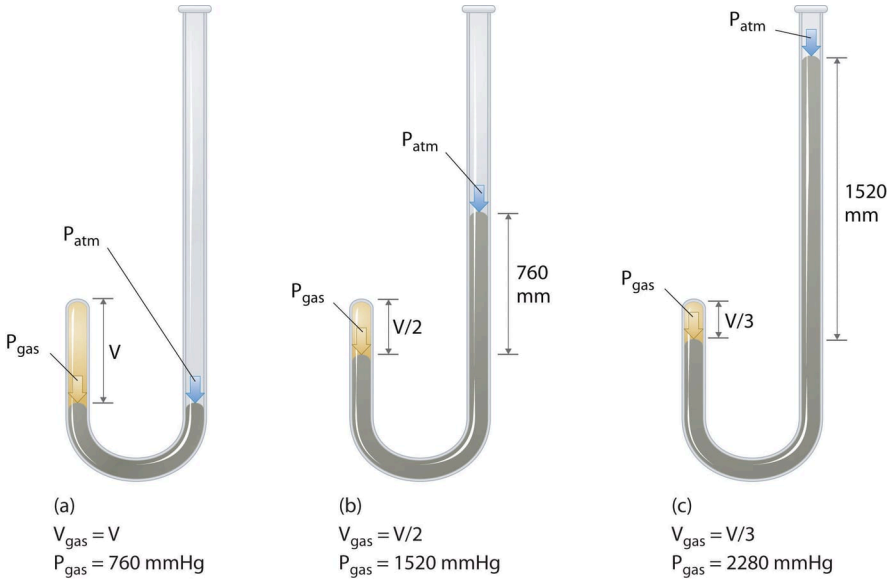


Figure 6.2.1: Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is *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.

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V:

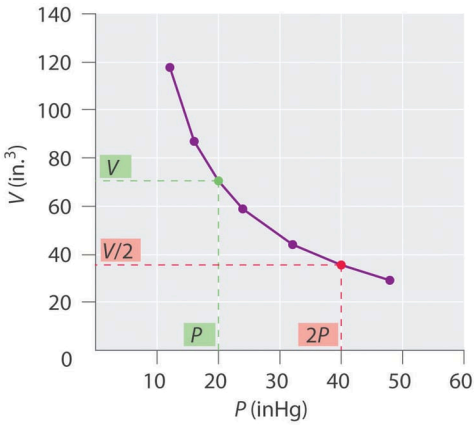
$$V = \frac{\text{const.}}{P} = \text{const.}\left(\frac{1}{P}\right) \tag{6.2.2}$$

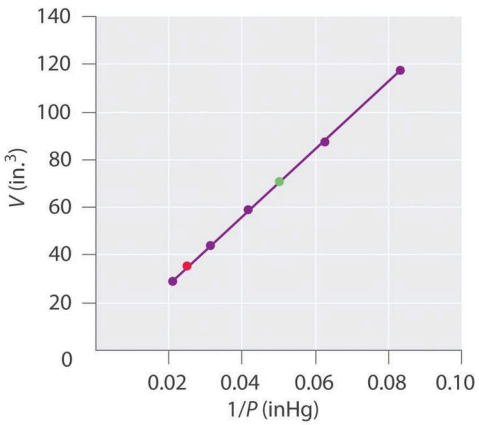
or

$$V \propto \frac{1}{P} \tag{6.2.3}$$

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 Equation 6.2.1 and Equation 6.2.3. Dividing both sides of Equation 6.2.1 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*.

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 6.2.2: 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.

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Boyle's Law: https://youtu.be/lu86VSupPO4

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 6.2.3).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 6.2.3 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 6.2.3, 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.

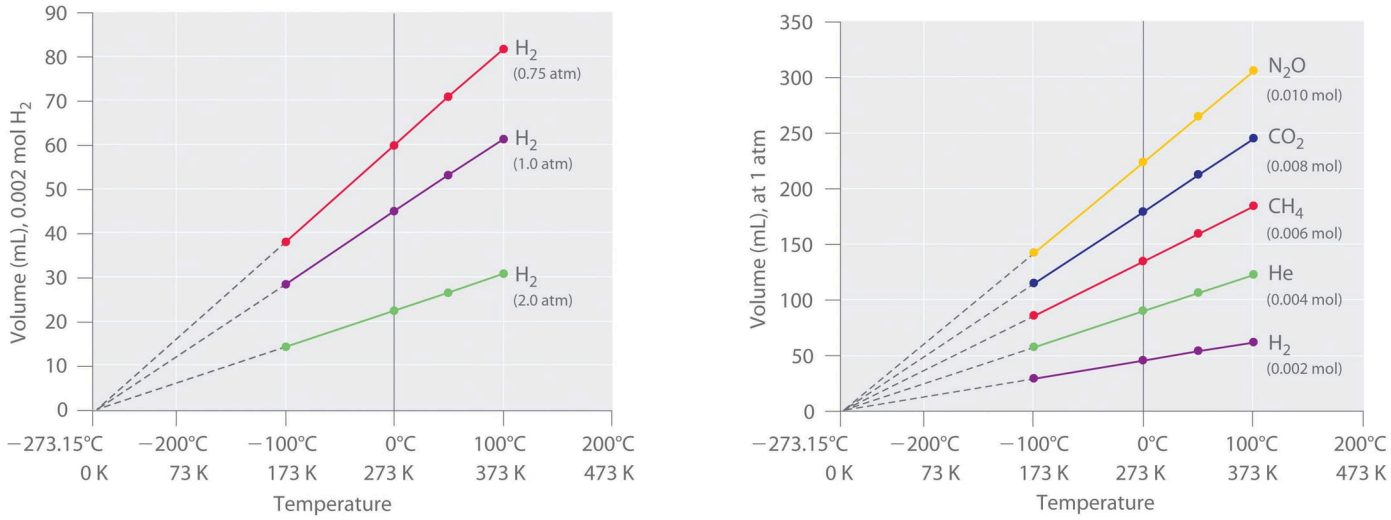


Figure 6.2.3: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to –100°C, and the broken lines show the extrapolation of the data to $V = 0$. 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.

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 6.2.3 is often referred to as Charles's law and is stated mathematically as

$$V = \text{const.}\ T \tag{6.2.4}$$

or

$$V \propto T \tag{6.2.5}$$

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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Charles's Law: https://youtu.be/NBf510ZnlR0

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 6.2.4). This is the historic "Avogadro's hypothesis."

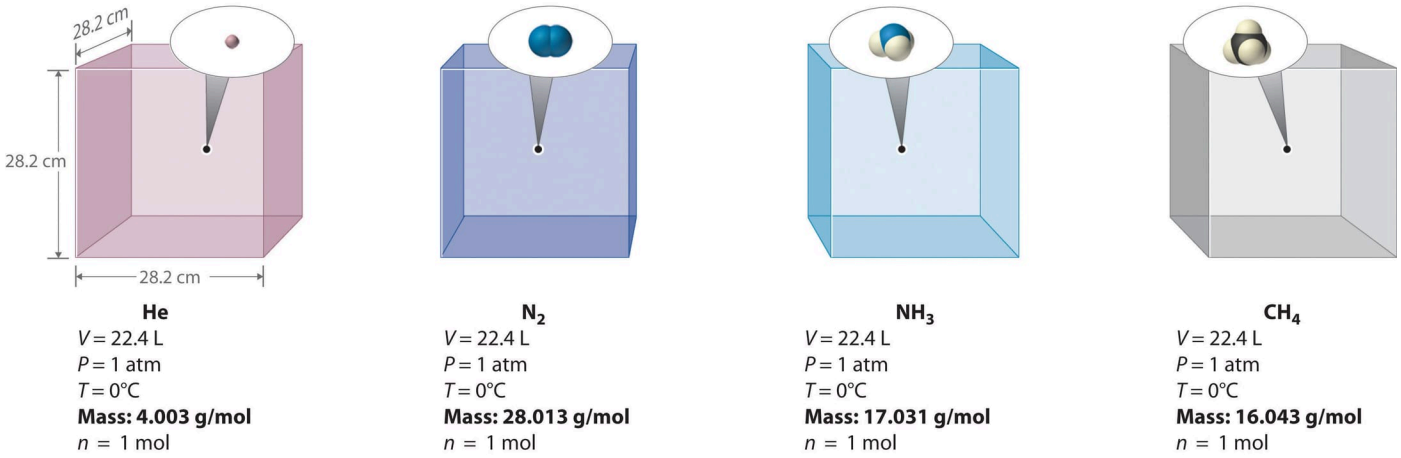


Figure 6.2.4: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas.

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,

$$V = \text{const.}\ (n) \tag{6.2.6}$$

or

$$V \propto .n@\ \text{constant T and P} \tag{6.2.7}$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.

Note

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 6.2.5. 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 6.2.5: 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.

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Avogadro's Law: https://youtu.be/dRY3Trl4T24

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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6.3: Combining the Gas Laws: The Ideal Gas Equation and the General Gas Equation

Learning Objectives

- 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 are as follows:

- **Boyle's law**

$$V \propto \frac{1}{P} \quad @ \text{ constant n and T} \tag{6.3.1}$$

- **Charles's law**

$$V \propto T \quad @ \text{ constant n and P} \tag{6.3.2}$$

- **Avogadro's law**

$$V \propto n \quad @ \text{ constant T and P} \tag{6.3.3}$$

Combining these three expressions gives

$$V \propto \frac{nT}{P} \tag{6.3.1}$$

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

$$V = \text{Cons.} \left(\frac{nT}{P}\right) \tag{6.3.2}$$

By convention, the proportionality constant in Equation 6.3.1 is called the gas constant, which is represented by the letter R. Inserting R into Equation 6.3.2 gives

$$V = \frac{Rnt}{P} = \frac{nRT}{P} \tag{6.3.3}$$

Clearing the fractions by multiplying both sides of Equation 6.3.4 by P gives

$$PV = nRT \tag{6.3.4}$$

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.

> **Note**
>
> 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

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \tag{6.3.5}$$

Because the product PV has the units of energy, R can also have units of J/(K•mol):

$$R = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \tag{6.3.6}$$

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**).

$$\text{STP:} \qquad T = 273.15\ \text{K and}\ P = 1\ \text{bar} = 10^5\ \text{Pa} \tag{6.3.4}$$

Please note that STP was defined differently in the part. 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 6.3.4:

$$V = \frac{nRT}{P} \tag{6.3.7}$$

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 6.3.1: 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 6.3.1

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 6.3.4) for *n*, we obtain

$$745\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 0.980\ \text{atm} \tag{6.3.5}$$

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:

$$T = 273 + 30 = 303\text{K} \tag{6.3.6}$$

Substituting these values into the expression we derived for *n*, we obtain

$$n = \frac{PV}{RT} = \frac{0.980\ \text{atm} \times 31150\ \text{L}}{0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 303\ \text{K}} = 1.23 \times 10^3\ \text{mol} \tag{6.3.7}$$

Exercise 6.3.1

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: 1.5 atm

In Example 6.3.1, 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 6.3.5.

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The Ideal Gas Law: https://youtu.be/rHGs23368mE

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:

$$\begin{matrix} \text{Initial condition } (i) & \text{Final condition}(f) \\ P_iV_i = n_iRT_i & P_fV_f = n_fRT_f \end{matrix} \tag{6.3.8}$$

Both equations can be rearranged to give:

$$R = \frac{P_iV_i}{n_iT_i} \qquad R = \frac{P_fV_f}{n_fT_f} \tag{6.3.9}$$

The two equations are equal to each other since each is equal to the same constant R. Therefore, we have:

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f} \tag{6.3.8}$$

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.

Example 6.3.2

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 6.3.1?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A. Use the results from Example 6.3.1 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:

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 × 103 mol	$n_f =$1.23 × 103 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 can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f} \tag{6.3.10}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$V_f = V_i \times \frac{T_f}{T_i} = 31150\ \text{L} \times \frac{263\ \text{K}}{303\ \text{K}} = 2.70 \times 10^4\ \text{L} \tag{6.3.11}$$

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 6.3.2

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: 0.52 L

Example 6.3.1 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 6.3.1 can be applied in *any* such case, as we demonstrate in Example 6.3.2 (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 6.3.3

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 5 (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 6.3.5.

Solution:

Prepare a table to determine which parameters change and which are held constant:

Initial	Final
$V_i = 0.406\ \text{L}$	$V_f = 0.406\ \text{L}$
$n_i = 0.025\ \text{mol}$	$n_f = 0.025\ \text{mol}$
$T_i = 25\ ^\circ\text{C} = 298\ \text{K}$	$T_i = 750\ ^\circ\text{C} = 1023\ \text{K}$
$P_i = 1.5\ \text{atm}$	$P_f = ?$

Both V and n are the same in both cases ($V_i = V_f, n_i = n_f$). Therefore, Equation can be simplified to:

$$P_i T_i = P_f T_f \tag{6.3.12}$$

By solving the equation for P_f, we get:

$$P_f = P_i \times \frac{T_i}{T_f} = 1.5\ \text{atm} \times \frac{1023\ \text{K}}{298\ \text{K}} = 5.1\ \text{atm} \tag{6.3.13}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

Exercise 6.3.3

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: 23.4 atm

In Example 6.3.1 and Example 6.3.2, 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.

Example 6.3.4

We saw in Example 6.3.1 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 6.3.5.

Solution:

Begin by setting up a table of the two sets of conditions:

Initial	Final
$P_i = 745 \text{ mmHg} = 0.980 \text{ atm}$	$P_f = 312 \text{ mmHg} = 0.411 \text{ atm}$
$T_i = 30 \text{ °C} = 303 \text{ K}$	$T_f = 750 - 30 \text{ °C} = 243 \text{ K}$
$n_i = 1.2 \times 10^3 \text{ mol}$	$n_i = 1.2 \times 10^3 \text{ mol}$
$V_i = 31150 \text{ L}$	$V_f = ?$

By eliminating the constant property (n) of the gas, Equation 6.3.8 is simplified to:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \tag{6.3.14}$$

By solving the equation for V_f, we get:

$$V_f = V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i} = 3.115 \times 10^4 \text{ L} \times \frac{0.980 \text{ atm}}{0.411 \text{ atm}}\frac{243 \text{ K}}{303 \text{ K}} = 5.96 \times 10^4 \text{ L} \tag{6.3.15}$$

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 6.3.4

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: 4.07×10^3

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Second Type of Ideal Gas Law Problems: https://youtu.be/WQDJOqddPI0

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

$$\frac{n}{V} = \frac{P}{RT} \tag{6.3.9}$$

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):

$$n = \frac{m}{M} \tag{6.3.10}$$

Substituting this expression for n into Equation 6.3.9 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{6.3.11}$$

Because m/V is the density d of a substance, we can replace m/V by d and rearrange to give

$$\rho = \frac{m}{V} = \frac{MP}{RT} \tag{6.3.12}$$

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).

Example 6.3.5

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 6.3.12 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$M = (4)(12.011) + (10)(1.0079) = 58.123\text{g/mol} \tag{6.3.16}$$

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:

$$P = 750\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 0.987\ \text{atm} \tag{6.3.17}$$

B Substituting these values into Equation 6.3.12 gives

$$\rho = \frac{58.123\ \text{g/mol} \times 0.987\ \text{atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298\ \text{K}} = 2.35\ \text{g/L} \tag{6.3.18}$$

Exercise 6.3.5

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: radon, 9.23 g/L; N_2, 1.17 g/L

A common use of Equation 6.3.12 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 6.3.6.

Example 6.3.6

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 6.3.12 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 6.3.12 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P} \tag{6.3.19}$$

Density is the mass of the gas divided by its volume:

$$\rho = \frac{m}{V} = \frac{0.289\text{g}}{0.17\text{L}} = 1.84\text{g/L} \tag{6.3.20}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K \tag{6.3.21}$$

$$P = 727\text{mmHg} \times \frac{1\text{atm}}{760\text{mmHg}} = 0.957\text{atm} \tag{6.3.22}$$

The molar mass of the unknown gas is thus

$$\rho = \frac{1.84\ \text{g/L} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 291\ \text{K}}{0.957\ \text{atm}} = 45.9 \text{g/mol} \tag{6.3.23}$$

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:

$$M(\text{NO}) = 14 + 16 = 30\ \text{g/mol} \tag{6.3.24}$$

$$M(\text{N}_2\text{O}) = (2)(14) + 16 = 44\ \text{g/mol} \tag{6.3.25}$$

$$M(\text{NO}_2) = 14 + (2)(16) = 46\ \text{g/mol} \tag{6.3.26}$$

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 6.3.6

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: 44 g/mol; CO_2

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Density and the Molar Mass of Gases: https://youtu.be/gnkGBsvUFVk

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: $\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f}$

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.

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6.4: Applications of the Ideal Gas Equation

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

For gases the density varies with the number of gas molecules in a constant volume. The ideal-gas equation can be manipulated to solve a variety of different types of problems. To determine the density, ρ, of a gas, we rearrange the equation to

$$\rho = \frac{n}{V} = \frac{P}{RT} \tag{6.4.1}$$

Density of a gas is generally expressed in g/L. Multiplication of the left and right sides of the equation by the molar mass (M) of the gas gives

$$\frac{g}{L} = \frac{PM}{RT} \tag{6.4.2}$$

This allows us to determine the density of a gas when we know the molar mass, or vice versa.

Example 6.4.1

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.

$$(248\ \text{Torr}) \times \frac{1\ \text{atm}}{760\ \text{Torr}} = 0.3263\ \text{atm} \tag{6.4.3}$$

$$18^{o}C + 273 = 291K \tag{6.4.4}$$

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:

$$PV = nRT \tag{6.4.5}$$

$$\rho = \frac{m}{V} \tag{6.4.6}$$

where ρ=density, m=mass, V=Volume

$$m = M \times n \tag{6.4.7}$$

where m=mass, M=molar mass, n=moles

*Now take the density equation.

$$\rho = \frac{m}{V} \tag{6.4.8}$$

*Keeping in mind $m = M \times n$...replace $(M \times n)$ for $mass$ within the density formula.

$$\rho = \frac{M \times n}{V} \tag{6.4.9}$$

$$\frac{\rho}{M} = \frac{n}{V} \tag{6.4.10}$$

*Now manipulate the Ideal Gas Equation

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT} \tag{6.4.11}$$

*(n/V) is in both equations.

$$\frac{n}{V} = \frac{\rho}{M} \tag{6.4.12}$$

$$\frac{n}{V} = \frac{P}{RT} \tag{6.4.13}$$

*Now combine them please.

$$\frac{\rho}{M} = \frac{P}{RT} \tag{6.4.14}$$

*Isolate density.

$$\rho = \frac{PM}{RT} \tag{6.4.15}$$

Step 4: Now plug in the information you have.

$$\rho = \frac{PM}{RT} \tag{6.4.16}$$

$$\rho = \frac{(0.3263 \text{ atm})(2 * 14.01 \text{ g/mol})}{(0.08206 Latm/Kmol)(291 \text{ K})} \tag{6.4.17}$$

$$\rho = 0.3828 \ g/L \tag{6.4.18}$$

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 6.4.1), 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 6.4.1: A hot air balloon is inflated partially with cold air from a gas-powered fan, before the propane burners are used for final inflation.

Note

- The density of a gas INCREASES with increasing pressure (Equation 6.4.1)
- The density of a gas DECREASES with increasing temperature (Equation 6.4.1)

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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.

Example 6.4.2

What volume of carbon dioxide gas is produced at STP by the decomposition of 0.150 g $CaCO_3$ via the equation:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \tag{6.4.19}$$

Solution

Begin by converting the mass of calcium carbonate to moles.

$$\frac{0.150\ g}{100.1\ g/mol} = 0.0015\ mol \tag{6.4.20}$$

The stoichiometry of the reaction dictates that the number of moles $CaCO_3$ decomposed equals the number of moles CO_2 produced. Use the ideal-gas equation to convert moles of CO_2 to a volume.

$$V = \frac{nRT}{R} = \frac{(0.0015\ mol)\left(0.08206\ \frac{L \cdot atm}{mol \cdot K}\right)(273.15\ K)}{1\ atm} = 0.0336\ L\ or\ 33.6\ mL \tag{6.4.21}$$

Example 6.4.3

A 3.00 L container is filled with $Ne_{(g)}$ at 770 mmHg at 27°C. A $0.633\ \text{g}$ sample of CO_2 vapor is then added. What is the partial pressure of 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 = 770mmHg --> 1.01 atm
- V = 3.00L
- n_{Ne}=?
- T = 27°C --> $300\ K$

Other Unknowns: n_{CO_2}= ?

$$n_{CO_2} = 0.633\ \text{g CO}_2 \times \frac{1\ \text{mol}}{44\ \text{g}} = 0.0144\ \text{mol CO}_2 \tag{6.4.22}$$

Step 2: After writing down all your given information, find the unknown moles of Ne.

$$n_{Ne} = \frac{PV}{RT} \tag{6.4.23}$$

$$n_{Ne} = \frac{(1.01\ \text{atm})(3.00\ \text{L})}{(0.08206\ atm\ L/mol\ K)(300\ \text{K})} \tag{6.4.24}$$

$$n_{Ne} = 0.123\ \text{mol} \tag{6.4.25}$$

Because the pressure of the container before the 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!

$$P_{Ne} = 1.01\ \text{atm} \tag{6.4.26}$$

Step 3: Now that have pressure for Ne, you must find the partial pressure for CO_2. Use the ideal gas equation.

$$\frac{P_{Ne}V}{n_{Ne}RT} = \frac{P_{CO_2}V}{n_{CO_2}RT} \tag{6.4.27}$$

but because both gases share the same Volume (V) and Temperature (T) and since the Gas Constant (R) is constants, all three terms cancel and can be removed them from the equation.

$$\frac{P}{n_{Ne}} = \frac{P}{n_{CO_2}} \tag{6.4.28}$$

$$\frac{1.01\ \text{atm}}{0.123\ \text{mol Ne}} = \frac{P_{CO_2}}{0.0144\ \text{mol CO}_2} \tag{6.4.29}$$

$$P_{CO_2} = 0.118 \text{ atm} \tag{6.4.30}$$

This is the partial pressure CO_2.

Step 4: Now find total pressure.

$$P_{total} = P_{Ne} + P_{CO_2} \tag{6.4.31}$$

$$P_{total} = 1.01 \text{ atm} + 0.118 \text{ atm} \tag{6.4.32}$$

$$P_{total} = 1.128 \text{ atm} \approx 1.13 \text{ atm (with appropriate significant figures)} \tag{6.4.33}$$

Example 6.4.4

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:

$$2S_{(s)} + 3O_{2(g)} + 2H_2O_{(l)} \rightarrow 2H_2SO_{4(aq)} \tag{6.4.34}$$

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:

mass of H_2SO_4 → moles H_2SO_4 → moles O_2 → liters O_2

A We begin by calculating the number of moles of H_2SO_4 in 1.00 ton:

$$\frac{907.18 \times 10^3 \text{ g } H_2SO_4}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } H_2SO_4 \tag{6.4.35}$$

We next calculate the number of moles of O_2 required:

$$9250 \text{ mol } H_2SO_4 \times \frac{3\text{mol } O_2}{2\text{mol } H_2SO_4} = 1.389 \times 10^4 \text{ mol } O_2 \tag{6.4.36}$$

B After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of O_2:

$$V = \frac{nRT}{P} = \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 3.43 \times 10^5 \text{ L} \tag{6.4.37}$$

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 6.4.4

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:

$$Fe_{(s)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + FeCl_{2(aq)} \tag{6.4.38}$$

How much iron (in kilograms) was needed to produce this volume of H_2 if the temperature was 30°C and the atmospheric pressure was 745 mmHg?

Answer: 68.6 kg of Fe (approximately 150 lb)

Example 6.4.5

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2NaN_3 \rightarrow 2Na_{(s)} + 3N_{2\ (g)} \tag{6.4.39}$$

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, as in Figure 6.4.4, 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 6.4.4, 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:

$$\frac{5.00\ \text{g NaN}_3}{(22.99 + 3 \times 14.01)\ \text{g/mol}} \times \frac{3\text{mol N}_2}{2\text{mol NaN}_3} = 0.115\ \text{mol N}_2 \tag{6.4.40}$$

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 6.4.4 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

$$(762 - 18.65)\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{atm}} = 743.4\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{atm}} = 0.978\ \text{atm}. \tag{6.4.41}$$

B Solving the ideal gas law for *V* and substituting the other quantities (in the appropriate units), we get

$$V = \frac{nRT}{P} = \frac{0.115\ \text{mol} \times 0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 294\ \text{K}}{0.978\ \text{atm}} = 2.84\ \text{L} \tag{6.4.42}$$

Exercise 6.4.5

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 $Zn(s) + 2\ HCl(aq) \rightarrow H_2(g) + ZnCl_2(aq)$. 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: 0.397 L

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Ideal Gas law Equation and Reaction Stoichiometry: https://youtu.be/8pPlW8MRhgI

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.

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6.5: Gases in Chemical Reactions

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.

Introduction

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. As a chemical engineer said to one of the authors, "Gases always go where you want them to, liquids sometimes do, but solids almost never do."

Example 6.5.1

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:

$$2S_{(s)} + 3O_{2(g)} + 2H_2O_{(l)} \rightarrow 2H_2SO_{4(aq)} \tag{6.5.1}$$

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:

mass of H_2SO_4 → moles H_2SO_4 → moles O_2 → liters O_2

A We begin by calculating the number of moles of H_2SO_4 in 1.00 ton:

$$\frac{907.18 \times 10^3 \text{ g } H_2SO_4}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } H_2SO_4 \tag{6.5.2}$$

We next calculate the number of moles of O_2 required:

$$9250 \text{ mol } H_2SO_4 \times \frac{3\text{mol } O_2}{2\text{mol } H_2SO_4} = 1.389 \times 10^4 \text{ mol } O_2 \tag{6.5.3}$$

B After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of O_2:

$$V = \frac{nRT}{P} = \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 3.43 \times 10^5 \text{ L} \tag{6.5.4}$$

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 6.5.1

In Example 5, we saw that 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:

$$Fe_{(s)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + FeCl_{2(aq)} \tag{6.5.5}$$

How much iron (in kilograms) was needed to produce this volume of H_2 if the temperature was 30°C and the atmospheric pressure was 745 mmHg?

Answer: 68.6 kg of Fe (approximately 150 lb)

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Ideal Gas law Equation and Reaction Stoichiometry: https://youtu.be/8pPlW8MRhgI

Collecting gases over water

As shown in Figure 6.5.1, a common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. Because the gas is less dense than liquid water, it bubbles to the top of the bottle, displacing the water. Eventually, all the water is forced out and the bottle contains only gas. If a calibrated bottle is used (i.e., one with markings to indicate the volume of the gas) and the bottle is raised or lowered until the level of the water is the same both inside and outside, then the pressure within the bottle will exactly equal the atmospheric pressure measured separately with a barometer ($P_{\text{bar.}}$).

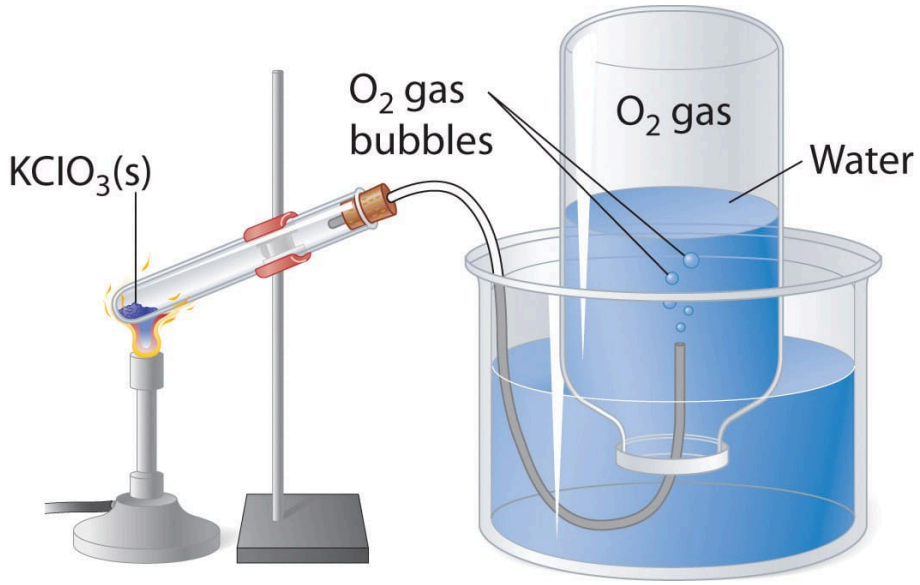


Figure 6.5.1: An Apparatus for Collecting Gases by the Displacement of Water

Remember, however, when calculating the amount of gas formed in the reaction, the gas collected inside the bottle is *not* pure. Instead, it is a mixture of the product gas and water vapor. All liquids (including water) have a measurable amount of vapor in equilibrium with the liquid because molecules of the liquid are continuously escaping from the liquid's surface, while other molecules from the vapor phase collide with the surface and return to the liquid. The vapor thus exerts a pressure above the liquid, which is called the liquid's ***vapor pressure***. In the case shown in Figure 6.5.1, the bottle is therefore actually filled with a mixture of O_2 and water vapor, and the total pressure is, by **Dalton's law** of partial pressures, the sum of the pressures of the two components:

$$P_{\text{tot}} = P_{\text{gas}} + P_{\text{H}_2\text{O}} = P_{\text{bar.}} \tag{6.5.6}$$

If we want to know the pressure of the gas generated in the reaction to calculate the amount of gas formed, we must first subtract the pressure due to water vapor from the total pressure. This is done by referring to tabulated values of the vapor pressure of water as a function of temperature (Table 6.5.1).

Table 6.5.1: Vapor Pressure of Water at Various Temperatures

T (°C)	*P* (in mmHg)
0	4.58
15	12.79
17	14.53
19	16.48
21	18.65
23	21.07
25	23.76
30	31.82
50	92.51
70	233.8
100	760.0

As shown in Figure 6.5.2, the vapor pressure of water increases rapidly with increasing temperature, and at the normal boiling point (100°C), the vapor pressure is exactly 1 atm. The methodology is illustrated in Example 6.5.2. The only gases that cannot be collected using this technique are those that readily dissolve in water (e.g., NH_3, H_2S, and CO_2) and those that react rapidly with

water (such as F_2 and NO_2).

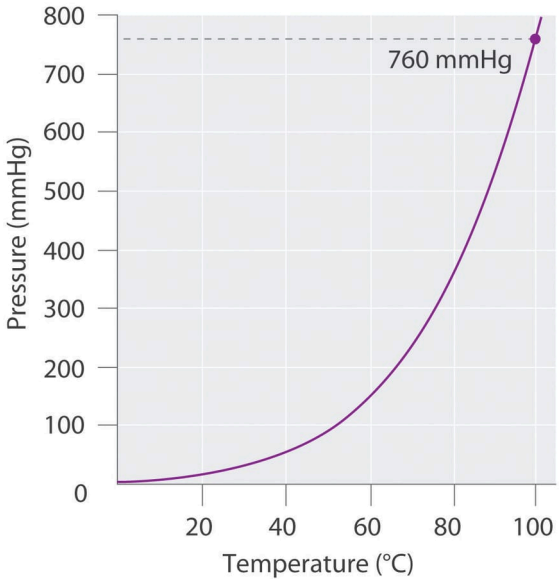


Figure $6.5.2$***:*** *A Plot of the Vapor Pressure of Water versus Temperature. The vapor pressure is very low (but not zero) at 0°C and reaches 1 atm = 760 mmHg at the normal boiling point, 100°C.*

Example $6.5.2$

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2NaN_3 \rightarrow 2Na_{(s)} + 3N_{2\ (g)} \tag{6.5.7}$$

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, as in Figure $6.5.1$, 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 $6.5.1$, 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:

$$\frac{5.00\ \text{g NaN}_3}{(22.99 + 3 \times 14.01)\ \text{g/mol}} \times \frac{3\text{mol N}_2}{2\text{mol NaN}_3} = 0.115\ \text{mol N}_2 \tag{6.5.8}$$

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 6.5.1 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

$$(762 - 18.65)\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{atm}} = 743.4\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{atm}} = 0.978\ \text{atm}. \tag{6.5.9}$$

B Solving the ideal gas law for *V* and substituting the other quantities (in the appropriate units), we get

$$V = \frac{nRT}{P} = \frac{0.115\ \text{mol} \times 0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 294\ \text{K}}{0.978\ \text{atm}} = 2.84\ \text{L} \tag{6.5.10}$$

Exercise 6.5.2

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 Zn(s) + 2 HCl(aq) → H_2(g) + $ZnCl_2$(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: 0.397 L

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

Collecting a Product Gas over Water: https://youtu.be/zFuy3t81vjQ

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.

Conceptual Problems

1. Why are so many industrially important reactions carried out in the gas phase?

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?

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

1. 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?
    1. $SO_2(g) + O_2(g) \rightarrow SO_3(g)$ given 2.4 mol of O_2
    2. $H_2(g) + Cl_2(g) \rightarrow HCl(g)$ given 0.78 g of H_2
    3. $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$ given 1.91 mol of O_2

- 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,

    1. what mass of CO is consumed?
    2. what volume of CO at STP is consumed?
    3. how much O_2 (in liters) at STP is used?
    4. what mass of carbon is consumed?
    5. how much iron metal (in grams) is produced?

- Complete decomposition of a sample of potassium chlorate produced 1.34 g of potassium chloride and oxygen gas.

    1. What is the mass of $KClO_3$ in the original sample?
    2. What mass of oxygen is produced?
    3. What is the volume of oxygen produced at STP?

- 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.

- 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.

Answers

1.
2.

3.
    1. 2.20 g $KClO_3$
    2. 0.863 g O_2
    3. 604 mL O_2
4.

5. Percent composition: 58.3% C, 4.93% H, 23.28% O, and 13.5% N; empirical formula: $C_{10}H_{10}O_3N_2$

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6.6: Mixtures of Gases

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:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{6.6.1}$$

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

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots = \sum_{i=1}^{n} P_i \tag{6.6.2}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

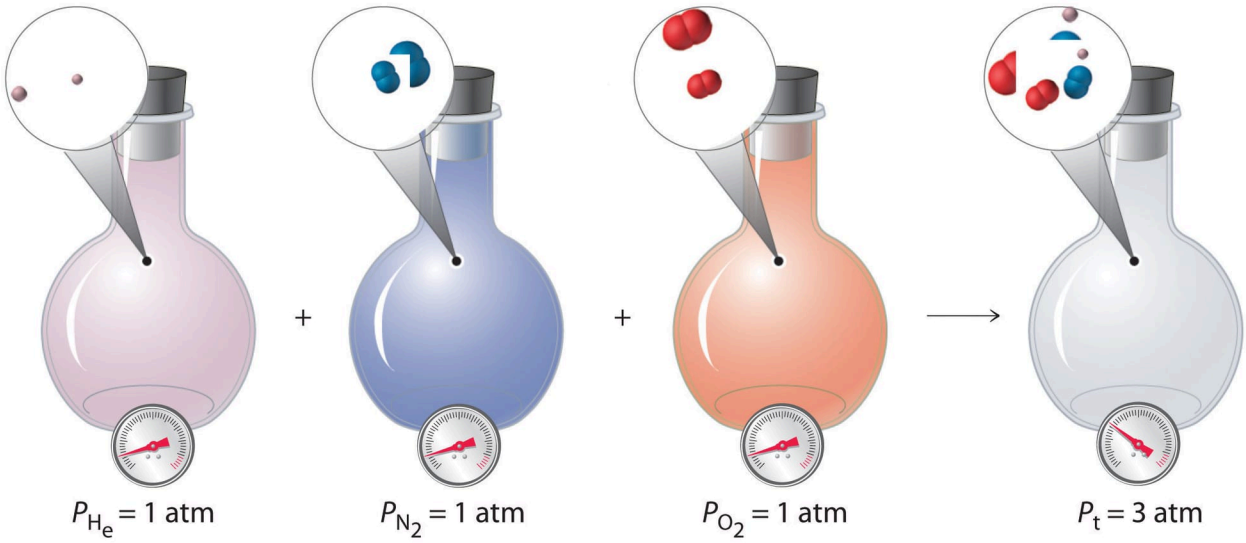


Figure 6.6.1: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right) \tag{6.6.3}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{6.6.4}$$

$$P_{tot} = \sum_{i=1}^{n} n_i\left(\frac{RT}{V}\right) \tag{6.6.5}$$

Equation 6.6.4 restates Equation 6.6.3 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 6.6.4 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 6.6.1.

Example 6.6.1

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 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

$$n_{\text{He}} = \frac{326.4 \text{ g}}{4.003 \text{ g/mol}} = 81.54 \text{ mol} \tag{6.6.6}$$

The number of moles of O_2 is

$$n_{\text{O}_2} = \frac{51.2 \text{ g}}{32.00 \text{ g/mol}} = 1.60 \text{ mol} \tag{6.6.7}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}}RT}{V} = \frac{81.54 \text{ mol} \times 0.08206 \dfrac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15 \text{ K}}{10.0 \text{ L}} = 196.2 \text{ atm} \tag{6.6.8}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{V} = \frac{1.60 \text{ mol} \times 0.08206 \dfrac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15 \text{ K}}{10.0 \text{ L}} = 3.85 \text{ atm} \tag{6.6.9}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85) \text{ atm} = 200.1 \text{ atm} \tag{6.6.10}$$

Exercise 6.6.1

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: $P_{CH_4} = 137 \ \ atm$; $P_{C_2H_6} = 13.4 \ \ atm$; $P_{tot} = 151 \ \ atm$

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 (X) 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}):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{6.6.11}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $x_A = 1.0$, then the sample is pure A, not a mixture. If $x_A = 0$, 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: $P_A = n_ART/V$ and $P_{tot} = n_tRT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_ART/V}{n_{tot}RT/V} = \frac{n_A}{n_{tot}} = x_A \tag{6.6.12}$$

Rearranging this equation gives

$$P_A = x_AP_{tot} \tag{6.6.13}$$

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 6.6.7, 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.

Example 6.6.2

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.

	Inhaled Air / mmHg	Exhaled Air / mmHg
P_{N_2}	597	568
P_{O_2}	158	116
P_{H_2O}	0.3	28
P_{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 6.6.7.

Solution:

The mole fraction of any gas A is given by

$$x_A = \frac{P_A}{P_{tot}} \tag{6.6.14}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of CO_2 is given as:

$$x_{CO_2} = \frac{48\ \text{mmHg}}{767\ \text{mmHg}} = 0.063 \tag{6.6.15}$$

The following table gives the values of x_A for the gases in the exhaled air.

Gas	Mole Fraction
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

Exercise 6.6.2

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

$$P_{CO_2} = 86 \text{ atm}, P_{N_2} = 2.7 \text{ atm}$$

YouTube Video

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Dalton's Law of Partial Pressures: https://youtu.be/y5-SbspyvBA

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.

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6.7: Kinetic-Molecular Theory of Gases

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:

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.

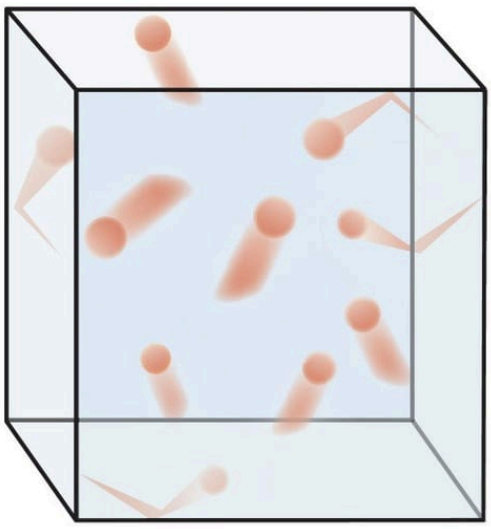


Figure 6.7.1 Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

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 Section 10.8, we explain how this theory must be modified to account for the behavior of real gases.

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 6.7.2).

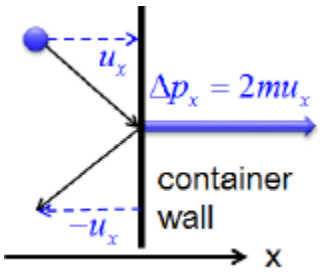


Figure 6.7.2 Momentum transfer (Impulse) from a molecule to the container wall as it bounces off the wall. u_x and Δp_x are the x component of the molecular velocity and the momentum transfered to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the molecule 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:

$$\Delta p_x = 2mu_x \tag{6.7.1}$$

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.

$$f \propto (u_x) \times \left(\frac{N}{V}\right) \tag{6.7.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mu_x^2 \tag{6.7.3}$$

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 :

$$P = \frac{N}{V} m\overline{u_x^2} \tag{6.7.4}$$

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, $\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}$. 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:

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2} \tag{6.7.5}$$

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*

$$\overline{e_K} = \frac{1}{2}m\overline{u^2} = \frac{3}{2}\frac{R}{N_A}T \tag{6.7.6}$$

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:

$$N_A\overline{e_K} = \frac{1}{2}M\overline{u^2} = \frac{3}{2}RT \tag{6.7.7}$$

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:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{6.7.8}$$

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:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{6.7.9}$$

In this equation, 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).

The equation 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 (v_p) 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 6.7.8 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 v_p increases.

Note

At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.

Example 6.7.1

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 6.7.6 to calculate the average speed and Equation 6.7.8 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:

$$v_{\text{av}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s} \tag{6.7.10}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\text{rms}} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}} = 6.2\ \text{m/s} \tag{6.7.11}$$

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, as you will learn in Chapter 14. 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 6.7.1. 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 6.7.1 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.

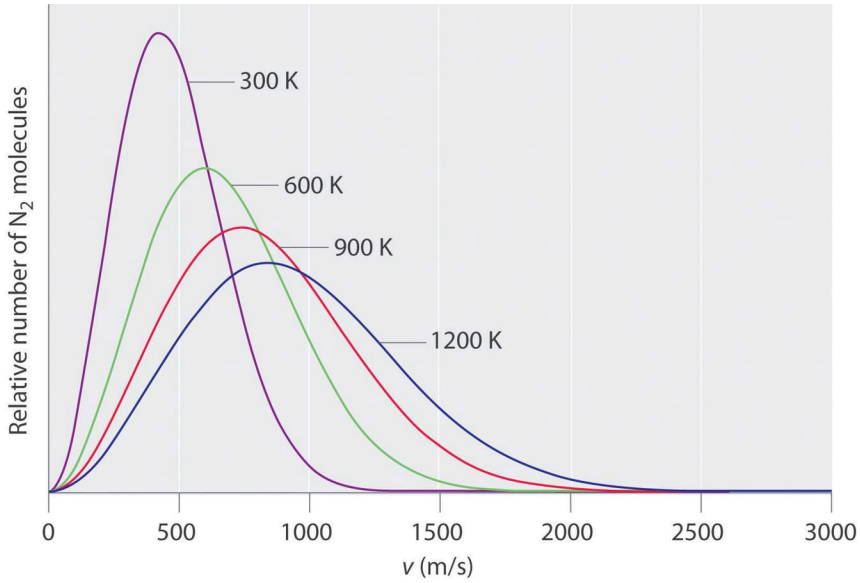


Figure 6.7.2 The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

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 6.7.2

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

1. average kinetic energy of the N_2 molecules?
2. rms speed of the N_2 molecules?
3. average speed of the N_2 molecules?
4. impact of each N_2 molecule on the wall of the container during a collision with the wall?
5. total number of collisions per second of N_2 molecules with the walls of the entire container?
6. number of collisions per second of N_2 molecules with each square centimeter of the container wall?
7. 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:

1. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
2. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
3. If the rms speed of the N_2 molecules increases, the average speed also increases.
4. If, on average, the particles are moving faster, then they strike the container walls with more energy.
5. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
6. 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.
7. 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 6.7.2

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

1. average kinetic energy of the He atoms?
2. rms speed of the He atoms?
3. average speed of the He atoms?
4. impact of each He atom on the wall of the container during a collision with the wall?
5. total number of collisions per second of He atoms with the walls of the entire container?
6. number of collisions per second of He atoms with each square centimeter of the container wall?
7. pressure of the He gas?

Answer: a. no change; b. no change; c. no change; d. no change; e. decreases; f. decreases; g. decreases

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Kinetic-Molecular Theory of Gases: https://youtu.be/9f83XAYfXAg

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:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T, \tag{6.7.12}$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}, \tag{6.7.13}$$

- **Kinetic molecular theory of gases:**

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \tag{6.7.14}$$

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.

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6.8: Gas Properties Relating to the Kinetic-Molecular Theory

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:

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}} \tag{6.8.1}$$

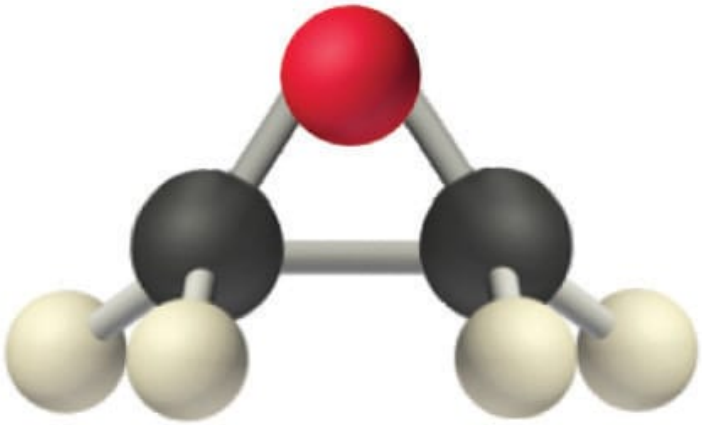


Figure 6.8.1 for ethylene oxide and helium. Helium (M = 4.00 g/mol) effuses much more rapidly than ethylene oxide (M = 44.0 g/mol). Because helium is less dense than air, helium-filled balloons "float" at the end of a tethering string. Unfortunately, rubber balloons filled with helium soon lose their 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.

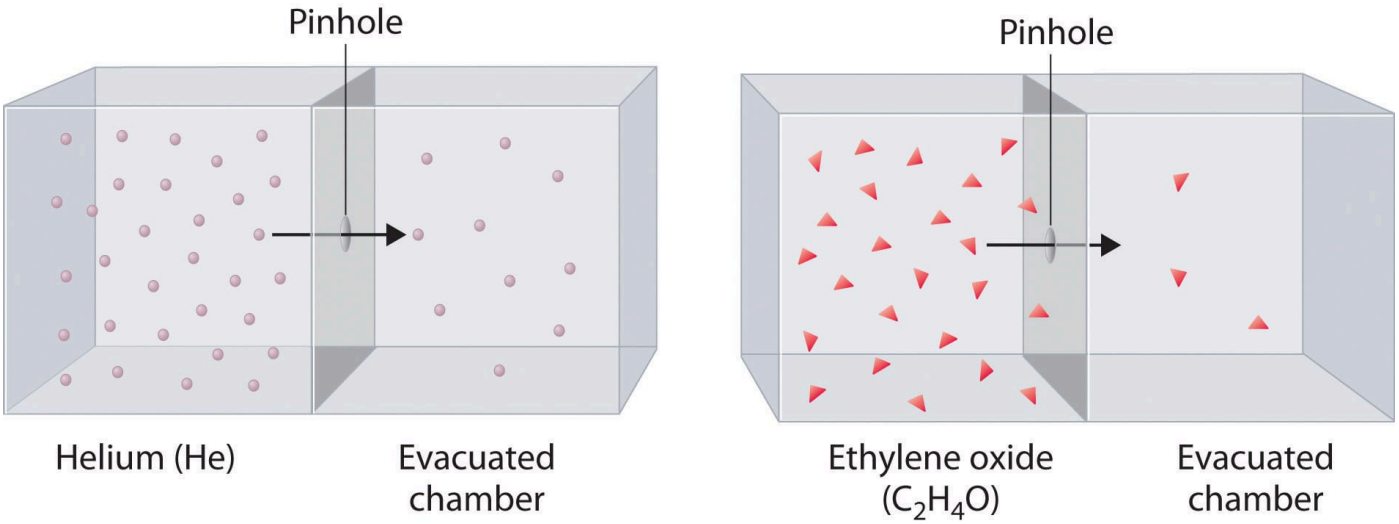


Figure 6.8.1: The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law.

Note

At a given temperature, heavier molecules move more slowly than lighter molecules.

Example 6.8.1

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 *n*th 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:

1. The molar mass of $^{238}UF_6$ is 238.05 + (6)(18.998) = 352.04 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 6.8.1:

$$\frac{\text{rate } ^{235}\text{UF}_6}{\text{rate } ^{238}\text{UF}_6} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} = 1.0043 \tag{6.8.2}$$

2. $=1.0043$

   Thus passing UF_6 containing a mixture of the two isotopes through a single porous barrier gives an enrichment of 1.0043, so after one step the isotopic content is (0.720%)(1.0043) = 0.723% $^{235}UF_6$.

3. **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

$$1.0043^n = \frac{0.990}{0.00720} = 137.50 \tag{6.8.3}$$

4. Taking the logarithm of both sides gives

$$n \ln(1.0043) = \ln(137.50) \tag{6.8.4}$$

$$n = \frac{\ln(137.50)}{\ln(1.0043)} = 1148 \tag{6.8.5}$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched ^{235}U. Figure 6.8.2 shows a small part of a system that is used to prepare enriched uranium on a large scale.



Figure 6.8.2: 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 6.8.1

Helium consists of two isotopes: ^{3}He (natural abundance = 0.000134%) and ^{4}He (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 ^{4}He by a process of gaseous effusion.

a. Calculate the ratio of the effusion rates of ^{3}He and ^{4}He and thus the enrichment possible in a single effusion step.
b. How many effusion steps are necessary to yield 99.0% pure ^{3}He?

Answer: a. ratio of effusion rates = 1.15200; one step gives 0.000154% ^{3}He; b. 96 steps

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:

$$KE = \frac{1}{2}\frac{M_{\mathrm{A}}}{N_A}v_{\mathrm{rms,A}}^2 = \frac{1}{2}\frac{M_{\mathrm{B}}}{N_A}v_{\mathrm{rms,B}}^2 \tag{6.8.6}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v_{\mathrm{rms,B}}^2}{v_{\mathrm{rms,A}}^2} = \frac{M_{\mathrm{A}}}{M_{\mathrm{B}}} \tag{6.8.7}$$

Taking the square root of both sides gives

$$\frac{v_{\mathrm{rms,B}}}{v_{\mathrm{rms,A}}} = \sqrt{\frac{M_{\mathrm{A}}}{M_{\mathrm{B}}}} \tag{6.8.8}$$

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 6.8.4 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 6.8.3 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.

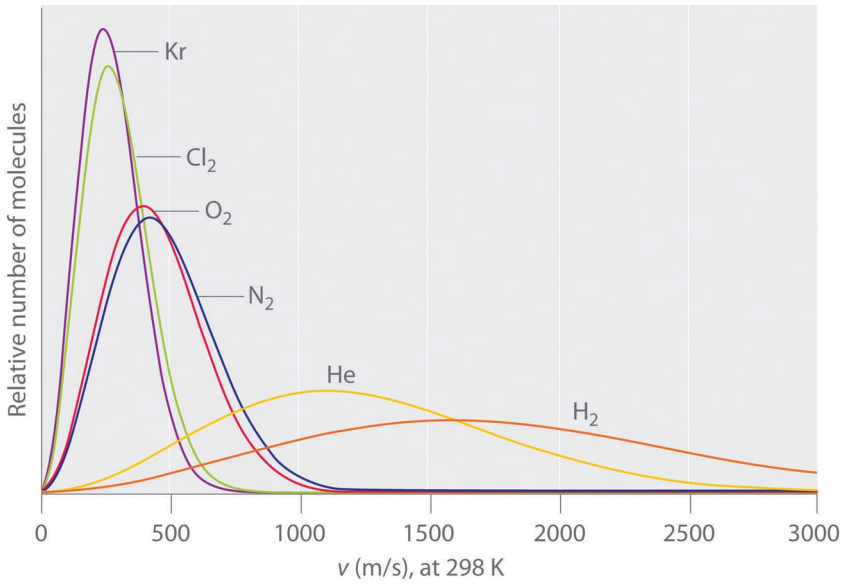


Figure 6.8.3: The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses

The lightest gases have a wider distribution of speeds and the highest average speeds.

Note

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 6.8.4.

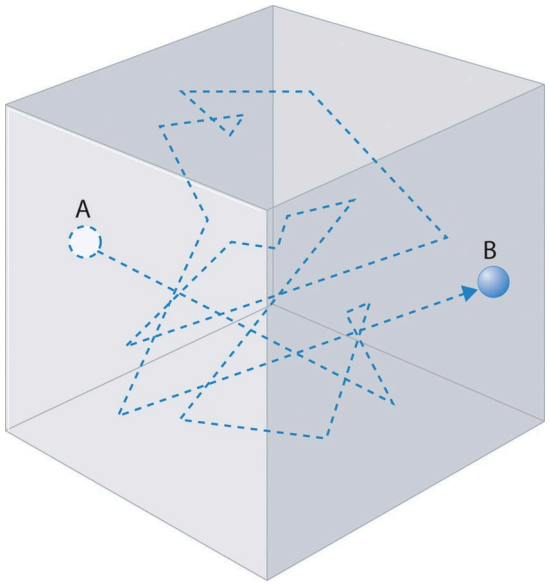


Figure 6.8.4: The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

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).

Note

The **denser** the gas, the **shorter** the mean free path.

Example 6.8.2

Calculate the rms speed of a sample of *cis*-2-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 6.8.5 to calculate the rms speed of the gas.

Solution:

To use Equation 6.8.4, 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

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.3145 \ \dfrac{\text{J}}{\text{K} \cdot \text{mol}} \times (20 + 273) \ \text{K}}{56.11 \times 10^{-3} \ \text{kg}}} = 361 \ \text{m/s} \tag{6.8.9}$$

or approximately 810 mi/h.

Exercise 6.8.2

Calculate the rms speed of a sample of radon gas at 23°C.

Answer: 1.82×10^2 m/s (about 410 mi/h)

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. In Section 10.8, we explore how the behavior of real gases differs from that of ideal gases.

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Graham's law of Diffusion and Effusion: https://youtu.be/9HO-qgh-iGI

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:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T, \tag{6.8.10}$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}, \tag{6.8.11}$$

- **Kinetic molecular theory of gases**:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \tag{6.8.12}$$

- **Graham's law for effusion:**

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_{\text{A}}}{M_{\text{B}}}} \tag{6.8.13}$$

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.

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6.9: Non-ideal (Real) Gases

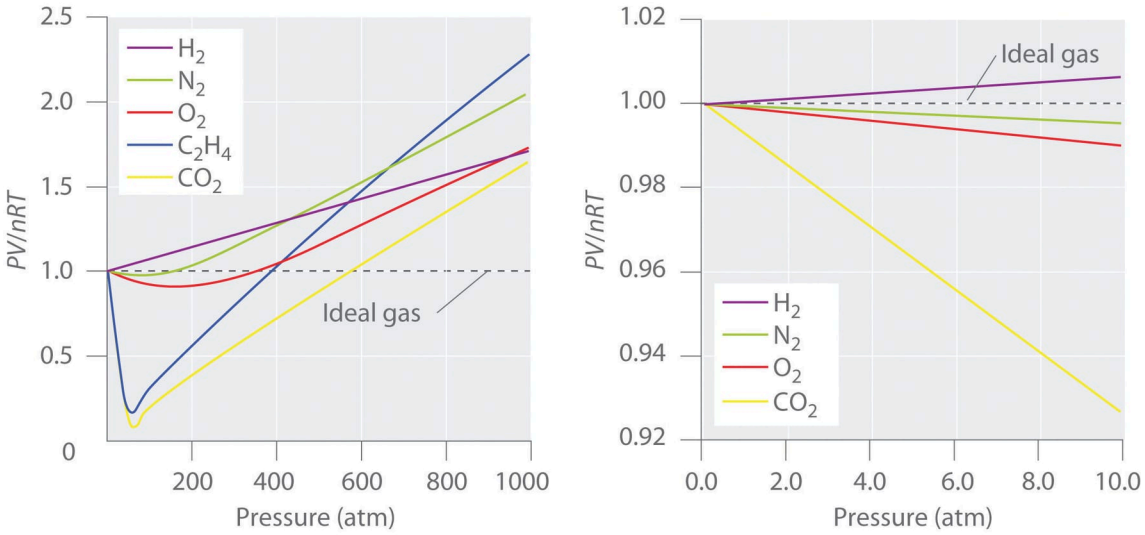
Learning Objectives

- 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 (part (a) in Figure $6.9.1$). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (part (b) in Figure $6.9.1$).



(a) *PV/nRT* at high pressures **(b) *PV/nRT* at low pressures**

Figure $6.9.1$: 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 $6.9.2$ 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.

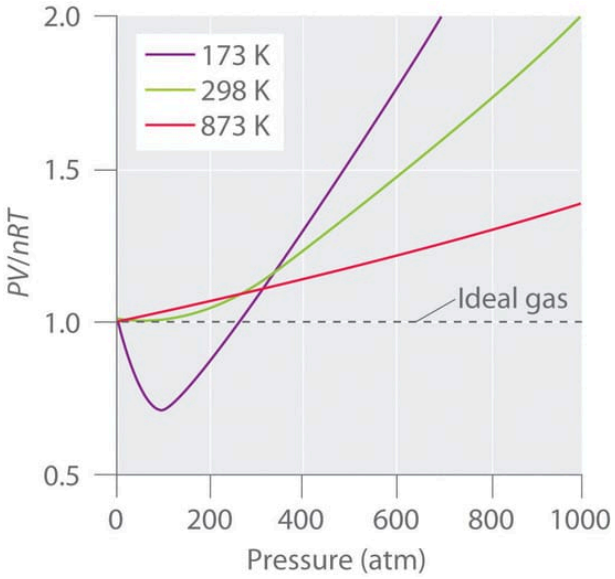


Figure $6.9.2$: The Effect of Temperature on the Behavior of Real Gases. A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

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 $6.9.3$). 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.

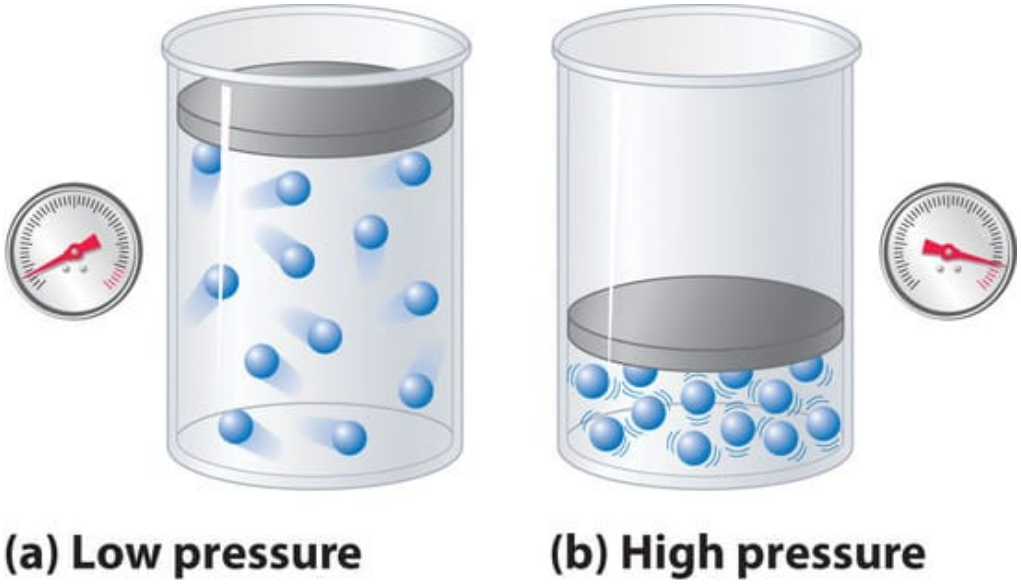


Figure $6.9.3$: The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the 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. Thus as shown in Figure $6.9.2$, 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,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{6.9.1}$$

a and *b* are empirical constants that are different for each gas. The values of a and b are listed in Table $6.9.1$ for several common gases.

Table $6.9.1$: van der Waals Constants for Some Common Gases (see Table A8 for more complete list)

Gas	a ($(L^2 \cdot atm)/mol^2$)	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 $6.9.1$ —$P + (an^2/V^2)$—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 $6.9.4$. The volume term—$V - nb$ —corrects for the volume occupied by the gaseous molecules.

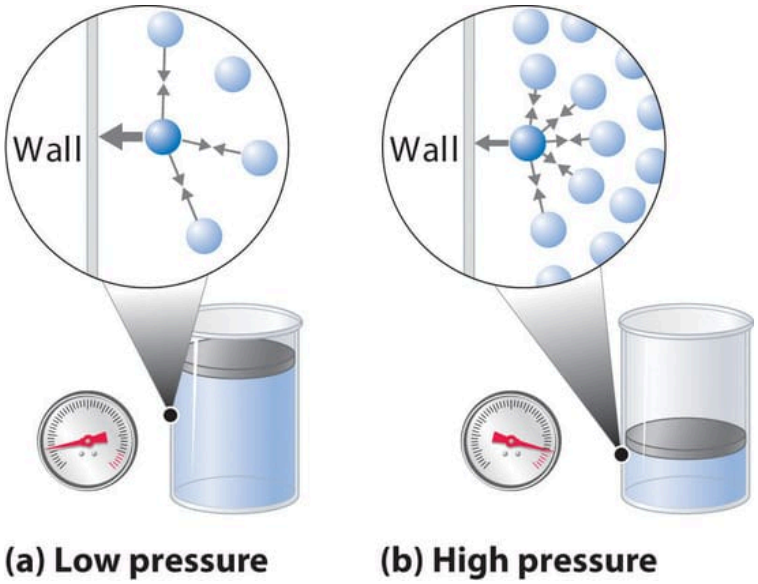


Figure 6.9.4: The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to 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 6.9.1

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 6.9.1. Use the van der Waals equation 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):

$$n = \frac{m}{M} = \frac{500\ \text{g}}{70.906\ \text{g/mol}} = 7.052\ \text{mol} \tag{6.9.2}$$

Using the ideal gas law and the temperature in kelvins (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} = \frac{7.052\ \text{mol} \times 0.08206 \dfrac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L}} = 43.1\ \text{atm} \tag{6.9.3}$$

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 6.9.1. Solving for *P* gives

$$\begin{aligned} P &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\ &= \frac{7.052\ \text{mol} \times 0.08206 \dfrac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L} - 7.052\ \text{mol} \times 0.0542 \dfrac{\text{L}}{\text{mol}}} - \frac{6.260 \dfrac{\text{L}^2\text{atm}}{\text{mol}^2} \times (7.052\ \text{mol})^2}{(4.00\ \text{L})^2} \\ &= 28.2\ \text{atm} \end{aligned} \tag{6.9.4}$$

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 6.9.1

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. 77 atm; b. 67 atm

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* 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 6.9.5: A Liquid Natural Gas Transport Ship

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure 6.9.5). 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**.

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7: THERMOCHEMISTRY

Petrucci: *General Chemistry*
Principles and Modern Applications

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7.1: Getting Started: Some Terminology

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 7.1.1). 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.

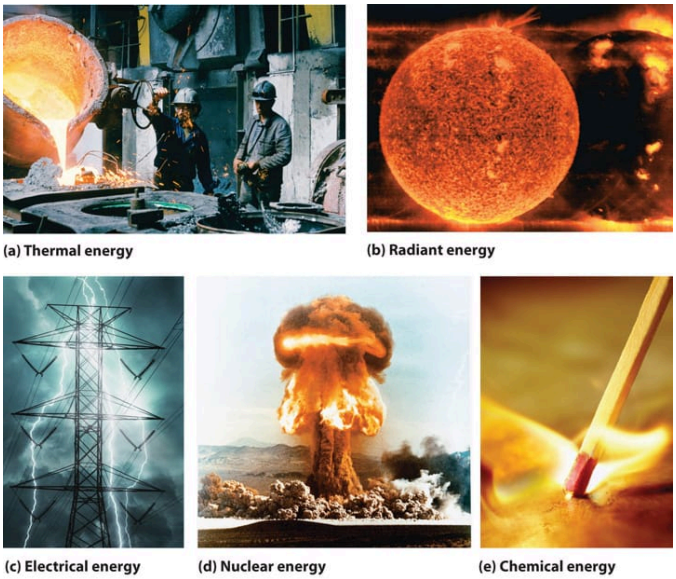


Figure 7.1.1: Forms of Energy. (a) *Thermal energy* results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, 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 7.1.2) 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.

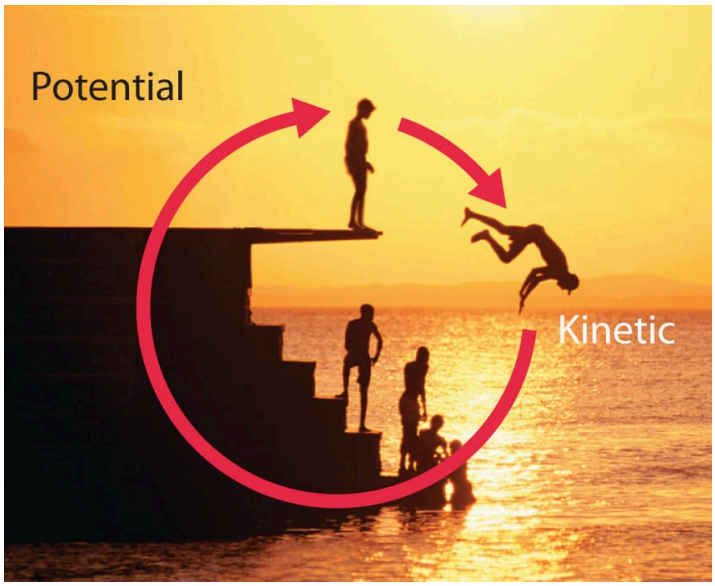


Figure 7.1.2: Interconversion of Forms of Energy. When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.

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.*

Kinetic and Potential Energy

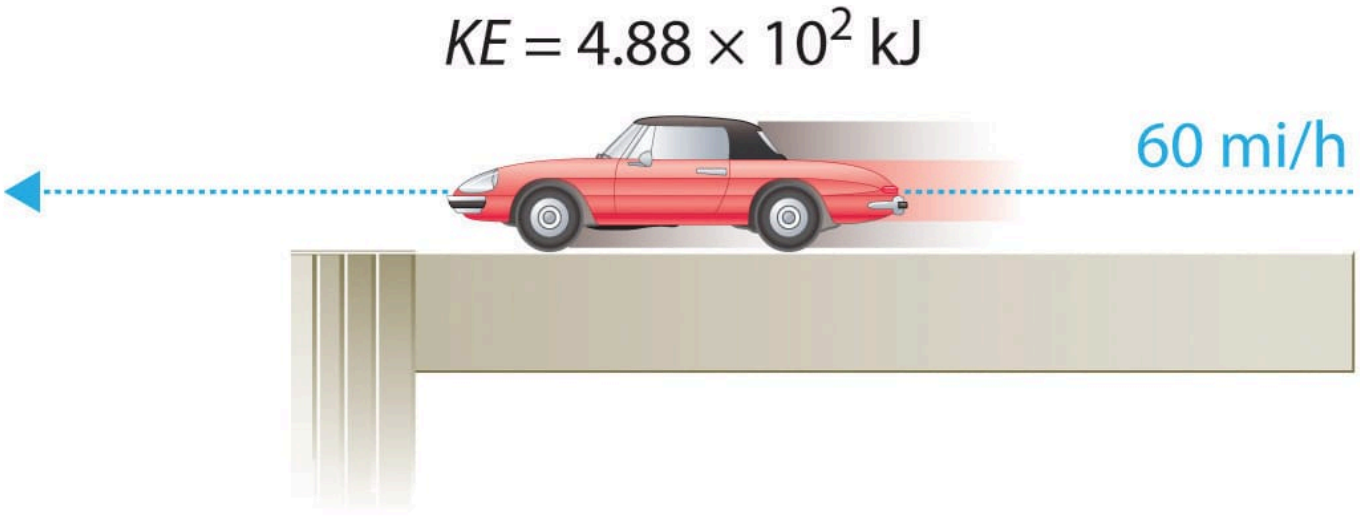
The kinetic energy of an object is related to its mass m and velocity v:

$$KE = \frac{1}{2}mv^2 \tag{7.1.4}$$

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

$$KE = \frac{1}{2}(1360kg)(26.8ms)^2 = 4.88 \times 10^5 g \cdot m^2 \tag{7.1.5}$$

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.



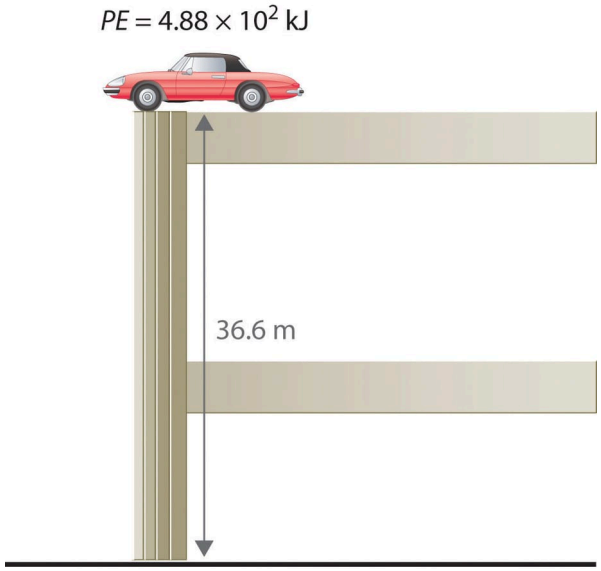
To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is $w = Fd$. According to Equation 7.1.2, 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:

$$PE = F\,d = m\,a\,d = m\,g\,h \tag{7.1.6a}$$

$$PE = (1360, Kg)\left(\frac{9.81\,m}{s^2}\right)(36.6\ m) = 4.88 \times 10^5\ \frac{Kg \cdot m}{s^2} \tag{7.1.6b}$$

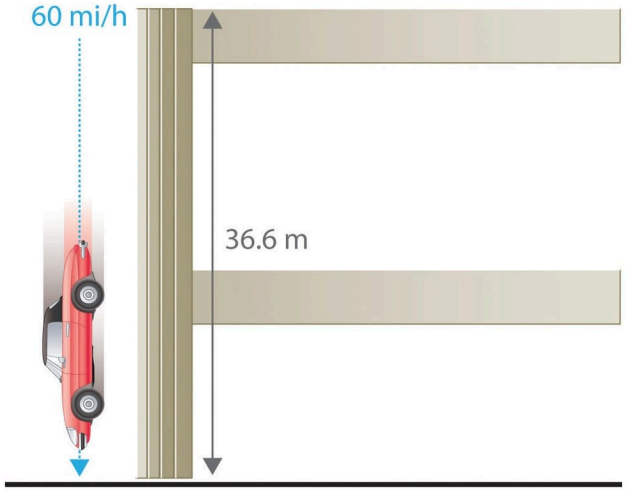
$$= 4.88 \times 10^5 J = 488\ kJ \tag{7.1.6c}$$

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.

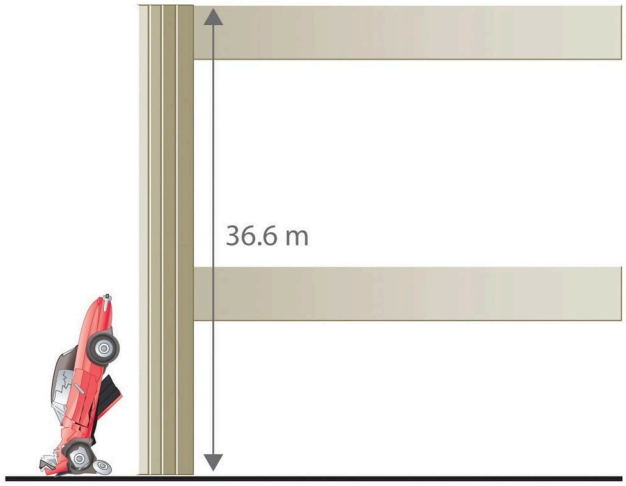


If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic 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.



$KE = 4.88 \times 10^2$ kJ



$PE = 0$ kJ, $KE = 0$

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:

$$1\ cal = 4.184\ J \text{ exactly} \tag{7.1.7a}$$

$$1\ J = 0.2390\ cal \tag{7.1.7b}$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information.

Example 7.1.1

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 7.1.4 to calculate the kinetic energy and Equation 7.1.6 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:

$$v = \left(\frac{100\ \cancel{mi}}{1\ \cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.61\ \cancel{km}}{1\ \cancel{mi}}\right)\left(\frac{1000\ m}{1\ \cancel{km}}\right) = 44.7\ m/s \tag{7.1.1}$$

The kinetic energy of the baseball is therefore

$$KE = 1492\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{44.7\ m}{s}\right)^2 = 1.49 \times 10^2\ \frac{kg \cdot m^2}{s^2} = 1.49 \times 10^2\ J \tag{7.1.2}$$

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

$$PE = 149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{9.81\ m}{s^2}\right)(247\ \cancel{ft})\left(\frac{0.3048\ m}{1\ \cancel{ft}}\right) = 1.10 \times 10^2\ \frac{kg \cdot m^2}{s^2} = 1.10 \times 10^2\ J \tag{7.1.3}$$

Exercise

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. 3.10×10^2 J
b. 65 J

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. Energy can be converted from one form to another, but the **law of conservation of energy** states that energy can be neither created nor destroyed. 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).

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7.2: Heat

Learning Objectives

- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of “hot” or “cold.” When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is “hot.” When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is “cold” (Figure 7.2.1). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

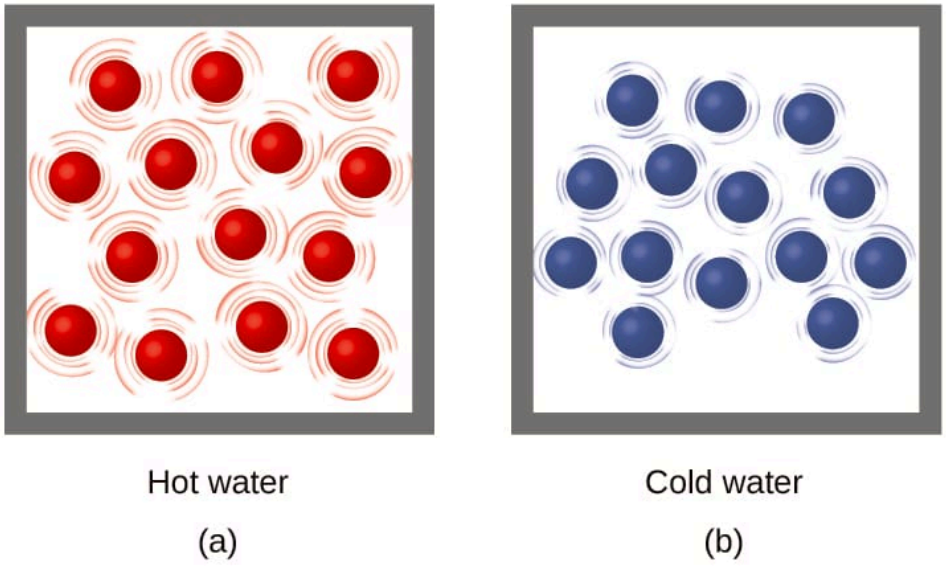
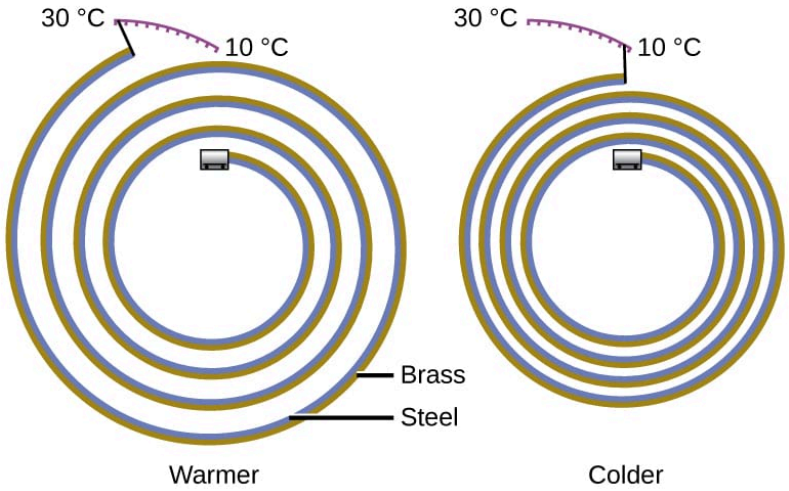


Figure 7.2.1: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 7.2.2. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.



(a)



(b)

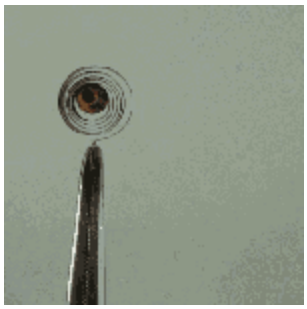


Figure 7.2.2: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by "dwstucke"/Flickr). (c) The demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.A bimetallic coil from a thermometer reacts to the heat from a lighter, by uncoiling and then coiling back up when the lighter is removed. Animation used with permission from Hustvedt (via Wikipedia)

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure 7.2.3).

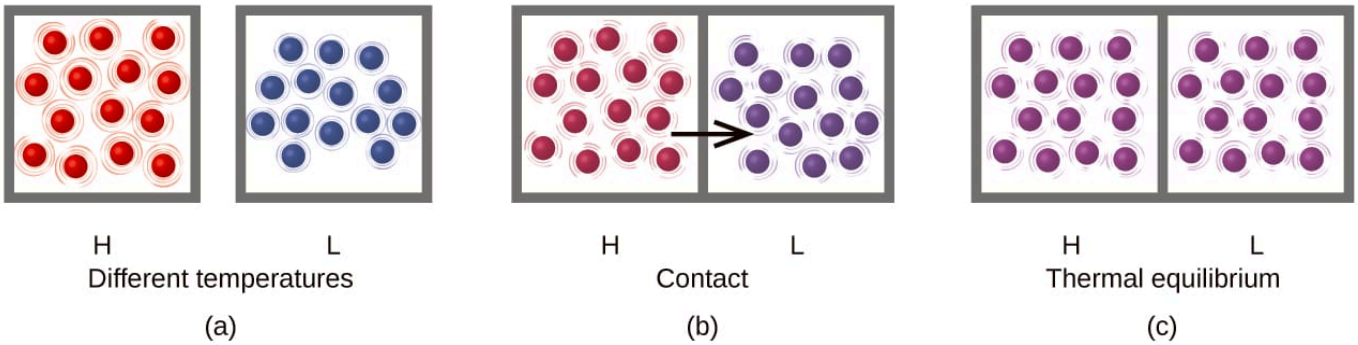


Figure 7.2.3: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an exothermic process. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure 7.2.4a). A reaction or change that absorbs heat is an endothermic process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



Figure 7.2.4: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons).

Historically, energy was measured in units of calories (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

Heat Capacity

We now introduce two concepts useful in describing heat flow and temperature change. The heat capacity (*C*) of a body of

matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin)

$$C = \frac{q}{\Delta T} \tag{7.2.1}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an *extensive* property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C

$$C_{\text{small pan}} = \frac{18,140J}{50.0\ °C} = 363\ J/°C \tag{7.2.2}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700\ J}{50.0\ °C} = 1814\ J/°C \tag{7.2.3}$$

The specific heat capacity (c) of a substance, commonly called its "specific heat," is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{m\Delta T} \tag{7.2.4}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{iron} = \frac{18,140\ J}{(808\ g)(50.0\ °C)} = 0.449\ J/g\ °C \tag{7.2.5}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{iron} = \frac{90,700J}{(4,040\ g)(50.0\ °C)} = 0.449\ J/g\ °C \tag{7.2.6}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 7.2.5).



Figure 7.2.5: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser).

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 (Equation 7.3.2) or mass (Equation 7.3.3):

$$q = nC_p\Delta T \tag{7.2.7}$$

where

- n is the number of moles of substance and
- C_p is the molar heat capacity (i.e., heat capacity per **mole** of substance)

$$q = mC_s\Delta T \tag{7.2.8}$$

where

The specific heats of some common substances are given in Table 7.2.1. 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.

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 7.2.1.

Table 7.2.1: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (state)	Specific Heat (J/g °C)
helium	He(*g*)	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376

Substance	Symbol (state)	Specific Heat (J/g °C)
ice	$H_2O(s)$	2.093 (at –10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
air	mixture	1.007
oxygen	$O_2(g)$	0.918
aluminum	Al(s)	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	Ar(g)	0.522
iron	Fe(s)	0.449
copper	Cu(s)	0.385
lead	Pb(s)	0.130
gold	Au(s)	0.129
silicon	Si(s)	0.712

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*.

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change}) \tag{7.2.9}$$

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \tag{7.2.10}$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read “delta T”) is the temperature change, $T_{final} - T_{initial}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{final} - T_{initial}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{final} - T_{initial}$ has a negative value, and the value of q is negative.

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The Movement of Heat in a Substance: https://youtu.be/gaJQYke-lVY

Example 7.2.1: Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \tag{7.2.11}$$
$$= (4.184\ \text{J/}\cancel{g}^{\circ}\text{C}) \times (800\ \cancel{g}) \times (85 - 20)^{\circ}\text{C} \tag{7.2.12}$$
$$= (4.184\ \text{J/}\cancel{g}^{\circ}\cancel{\text{C}}) \times (800\ \cancel{g}) \times (65)^{\circ}\cancel{\text{C}} \tag{7.2.13}$$
$$= 210,000\ \text{J} (= 210\ \text{kJ}) \tag{7.2.14}$$

Because the temperature increased, the water absorbed heat and q is positive.

Exercise 7.2.1

How much heat, in joules, must be added to a $5.00 \times 10^2\ \ g$ iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer:

$5.05 \times 10^4\ \ J$

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example 7.2.2: Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

$$q = c \times m \times \Delta T = c \times m \times (T_{final} - T_{initial}) \tag{7.2.15}$$

Substituting the known values:

$$6,640\ J = c \times (348\ g) \times (43.6 - 22.4)\ ^{\circ}C \tag{7.2.16}$$

Solving:

$$c = \frac{6,640\ J}{(348\ g) \times (21.2^{\circ}C)} = 0.900\ J/g\ ^{\circ}C \tag{7.2.17}$$

Comparing this value with the values in Table 7.2.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Exercise 7.2.2

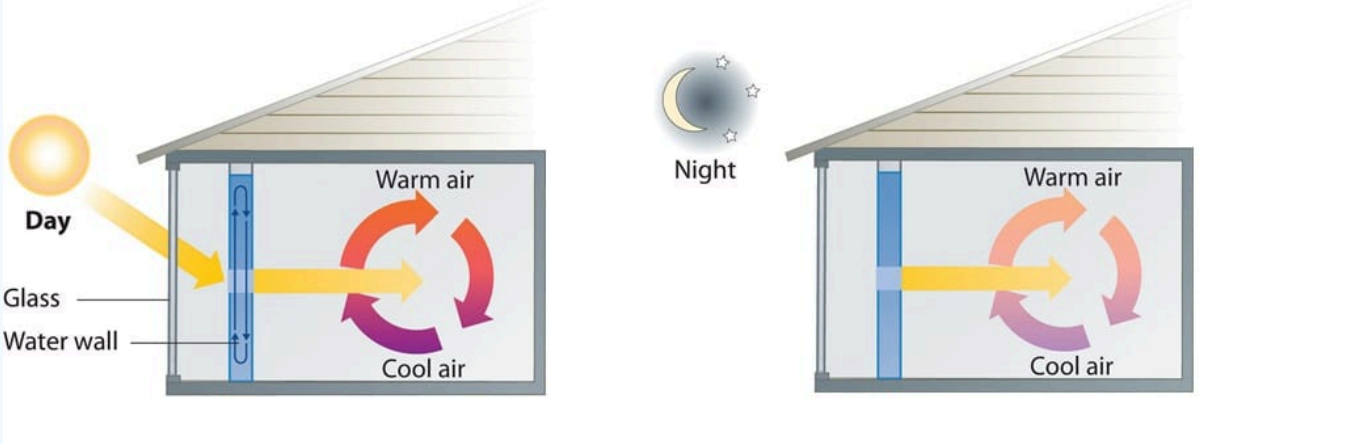
A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer

$c = 0.45\ \ J/g\ \ ^\circ C$; the metal is likely to be iron from checking Tabel 7.2.1

Example 7.2.3: 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 Δ*T* for the water.
B. Determine the amount of heat absorbed by substituting values for *m*, C_s, and Δ*T* into Equation 7.3.1.

Solution:

A The mass of water is

$$mass\ of\ H_2O = 400\ \cancel{L}\left(\frac{1000\ \cancel{mL}}{1\ \cancel{L}}\right)\left(\frac{0.998\ g}{1\ \cancel{mL}}\right) = 3.99 \times 10^5 g\ H_2O \tag{7.2.18}$$

The temperature change (Δ*T*) is 38.0°C – 22.0°C = +16.0°C.

B From Table 7.2.1, the specific heat of water is 4.184 J/(g•°C). From Equation 7.3.3, the heat absorbed by the water is thus

$$q = mC_s\Delta T = \left(3.99X10^5\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)\left(16.0\ \cancel{^oC}\right) = 2.67 \times 10^7 J = 2.67 \times 10^4 kJ \tag{7.2.19}$$

Both q and ΔT are positive, consistent with the fact that the water has absorbed energy.

Exercise 7.2.3: 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 7.2.1.

Answer

2.7×10^4 kJ (Even though the mass of sandstone is more than six times the mass of the water in Example 7.2.1, the amount of thermal energy stored is the same to two significant figures.)

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:

$$q_{cold} + q_{hot} = 0 \tag{7.2.20}$$

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:

$$q_{cold} = -q_{hot} \tag{7.2.21}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

The amount of heat lost by a warmer object equals the amount of heat gained by a cooler object.

Substituting for q from Equation 7.3.2 gives

$$[mC_s\Delta T]_{cold} + [mC_s\Delta T]_{hot} = 0 \tag{7.2.22}$$

which can be rearranged to give

$$[mC_s\Delta T]_{cold} = -[mC_s\Delta T]_{hot} \tag{7.2.23}$$

When two objects initially at different temperatures are placed in contact, we can use Equation 7.3.7 to calculate the final temperature if we know the chemical composition and mass of the objects.

Example 7.2.2: 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 7.3.7 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 7.3.7 to solve this problem, remembering that ΔT is defined as $T_{final} - T_{initial}$:

$$[mC_s\,(T_{final}-T_{initial})]_{Cu}+[mC_s\,(T_{final}-T_{initial})]_{H_2O}=0 \tag{7.2.24}$$

Substituting the data provided in the problem and Table 7.2.1 gives

$$[(30\ g)\,(0.385\ J)\,(T_{final}-T_{initial})]_{Cu}+[mC_s\,(T_{final}-T_{initial})]_{H_2O}=0 \tag{7.2.25}$$

$$T_{final}\,(11.6\ J/^oC)-924\ J+T_{final}\,(418.4\ J/^oC)-11,300\ J \tag{7.2.26}$$

$$T_{final}\,(430\ J/\,(g\cdot^o C))=-12,224\ J \tag{7.2.27}$$

$$T_{final}=-28.4\ ^oC \tag{7.2.28}$$

Exercise 7.2.2a: 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: 80.0°C

Exercise 7.2.2b: 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: 90.6°C

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7.3: Heats of Reactions and Calorimetry

Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data
- To use calorimetric data to calculate enthalpy changes.

Measuring Heat Flow

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process.

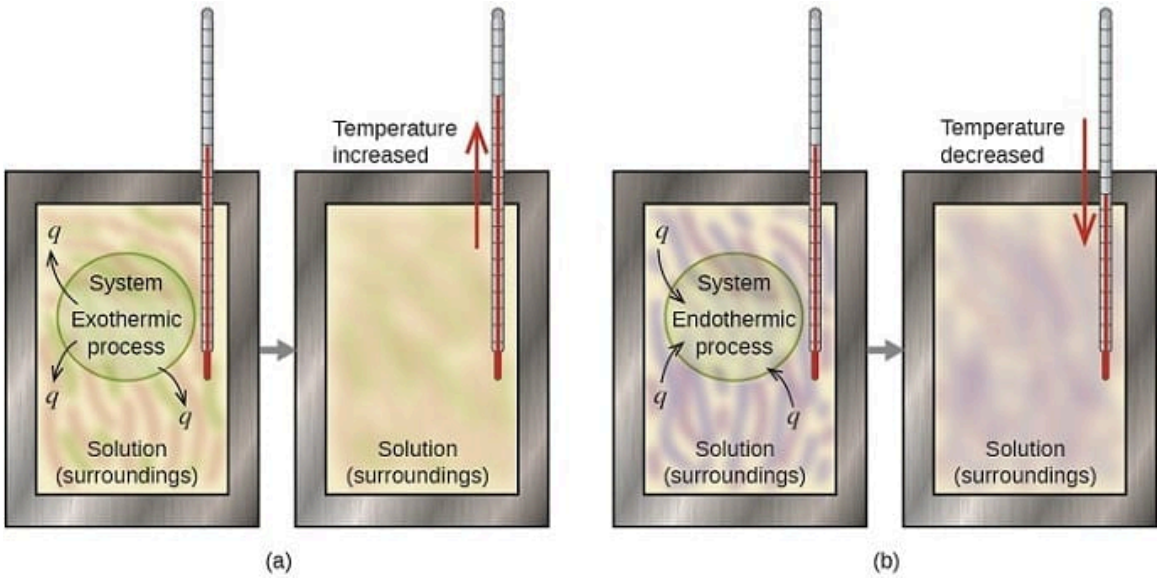


Figure 7.3.1: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system. (CC-BY; OpenStax).

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.

Note

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.

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 7.3.2), 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).

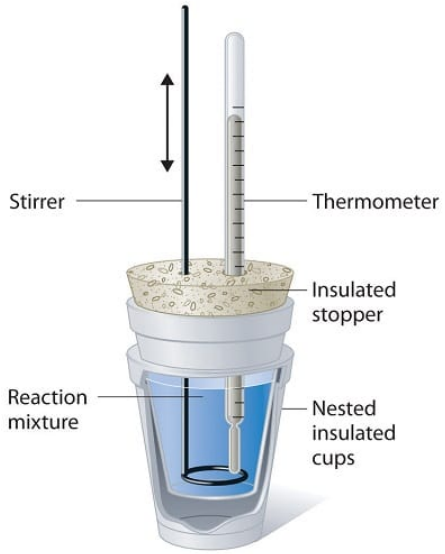


Figure 7.3.2: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

Before we practice calorimetry problems involving chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure 7.3.4). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0 \tag{7.3.1}$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}} \tag{7.3.2}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{substance\ M}$ and $q_{substance\ W}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{\text{substance M}}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W.

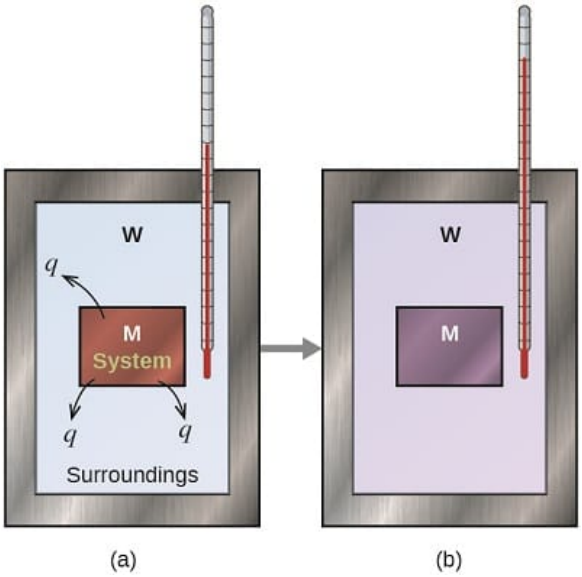


Figure 7.3.4: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Heat Transfer between Substances at Different Temperatures

A 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the surroundings, then heat given off by rebar = –heat taken in by water, or:

$$q_{\text{rebar}} = -q_{\text{water}} \tag{7.3.3}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}} \tag{7.3.4}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}}) \tag{7.3.5}$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449\ \text{J/g °C})(360\text{g})(42.7°\text{C} - T_{\text{i,rebar}}) = (4.184\ \text{J/g °C})(425\ \text{g})(42.7°\text{C} - 24.0°\text{C}) \tag{7.3.6}$$

$$T_{\text{i,rebar}} = \frac{(4.184\ \text{J/g °C})(425\ \text{g})(42.7°\text{C} - 24.0°\text{C})}{(0.449\ \text{J/g °C})(360\ \text{g})} + 42.7°\text{C} \tag{7.3.7}$$

Solving this gives Ti,rebar= 248 °C, so the initial temperature of the rebar was 248 °C.

Exercise 7.3.1A

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer:

The initial temperature of the copper was 335.6 °C.

Exercise 7.3.1B

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer:

The final temperature (reached by both copper and water) is 38.8 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, heat given off by metal = –heat taken in by water, or:

$$q_{\text{metal}} = -q_{\text{water}} \tag{7.3.8}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}}) \tag{7.3.9}$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7\text{ g})(28.5°\text{C} - 100.0°\text{C}) = -(4.18\text{ J/g °C})(60.0\text{ g})(28.5°\text{C} - 22.0°\text{C}) \tag{7.3.10}$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184\text{ J/g °C})(60.0\text{ g})(6.5°\text{C})}{(59.7\text{ g})(-71.5°\text{C})} = 0.38\text{ J/g °C} \tag{7.3.11}$$

Comparing this with values in Table T4, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise 7.3.2

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer

$$c_{metal} = 0.13 \ \ J/g \ \ ^\circ C$$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the "system"), q_{reaction}, plus the heat absorbed or lost by the solution (the "surroundings"), q_{solution}, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0 \tag{7.3.12}$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -q_{\text{solution}} \tag{7.3.13}$$

This concept lies at the heart of all calorimetry problems and calculations. Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mC_s\Delta T \tag{7.3.14}$$

The use of a constant-pressure calorimeter is illustrated in Example 7.3.3.

Example 7.3.3

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 7.3.1.
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

$$(100.0\ mL\ H2O)\left(0.9969\ g/\cancel{mL}\right) + 5.03\ g\ KOH = 104.72\ g \tag{7.3.15}$$

The temperature change is (34.7°C − 23.0°C) = +11.7°C.

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

$$q_{calorimater} = mC_s\Delta T = \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)(11.7\ ^oC) = 5130\ J = 5.13\ lJ \tag{7.3.16}$$

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 7.3.1, 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}—the heat released when dissolving 1 mol of KOH:

$$\Delta H_{soln} = \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right) = -57.2\ kJ/mol \tag{7.3.17}$$

Exercise 7.3.3

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 7.3.3, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer: 16.6 kJ/mol

YouTube Video

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Conservation of Energy: Coffee Cup Calorimetry: https://youtu.be/FwQcc17PN0k

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 7.3.3). 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.

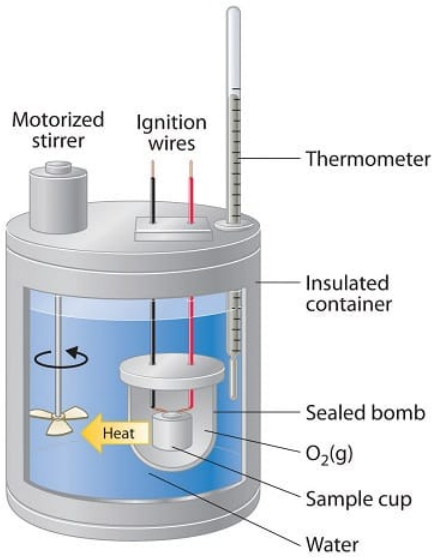


Figure 7.3.3: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released 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 (Δ*H*); ΔU is related to Δ*H* 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 7.3.18, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{7.3.18}$$

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 ΔH_{comb} = −26.38 kJ/g). This value and the measured increase in temperature of the calorimeter can be used in Equation ??? to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example 7.3.4.

YouTube Video

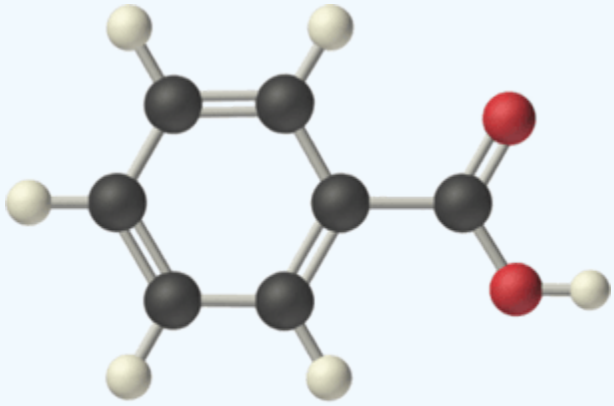
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Video* 7.3.1*: Video of view how a bomb calorimeter is prepared for action.

Example 7.3.4: 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 7.3.2 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 7.3.2 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:

$$q_{comb} = \left(0.579 \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) = -15.3\ kJ \tag{7.3.19}$$

From Equation 7.3.2,

$$-C_{bomb} = \frac{q_{comb}}{\Delta T} = \frac{-15.3\ kJ}{2.08\ ^oC} = -7.34\ kJ/^oC \tag{7.3.20}$$

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:

$$q_{comb} = -C_{bomb}\Delta T = (-7.34\ kJ/^oC)\,(3.64\ ^oC) = -26.7\ kJ \tag{7.3.21}$$

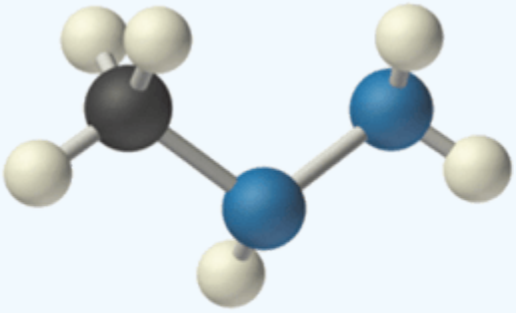
Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\Delta H_{comb} = \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) = -2780\ kJ/mol = 2.78 \times 10^3\ kJ/mol \tag{7.3.22}$$

This result is in good agreement (< 1% error) with the value of ΔH_{comb} = −2803 kJ/mol that calculated using enthalpies of formation.

Exercise 7.3.4: 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: -1.30×10^3 kJ/mol

YouTube Video

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Conservation of Energy: Bomb Calorimetry: https://youtu.be/SSNZGgwYBsQ

Summary

- 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 ΔH values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

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.

Contributors and Attributions

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7.4: Work

Learning Objectives

- To know the relationship between energy, work, and heat.

One definition of energy is the capacity to do work. There are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will consider only mechanical work and focus on the work done during changes in the pressure or the volume of a gas.

Mechanical Work

The easiest form of work to visualize is mechanical work (Figure 7.4.1), which is the energy required to move an object a distance d when opposed by a force F, such as gravity:

$$w = F\,d \tag{7.4.1}$$

with

- w is work
- F is opposing force
- d is distance

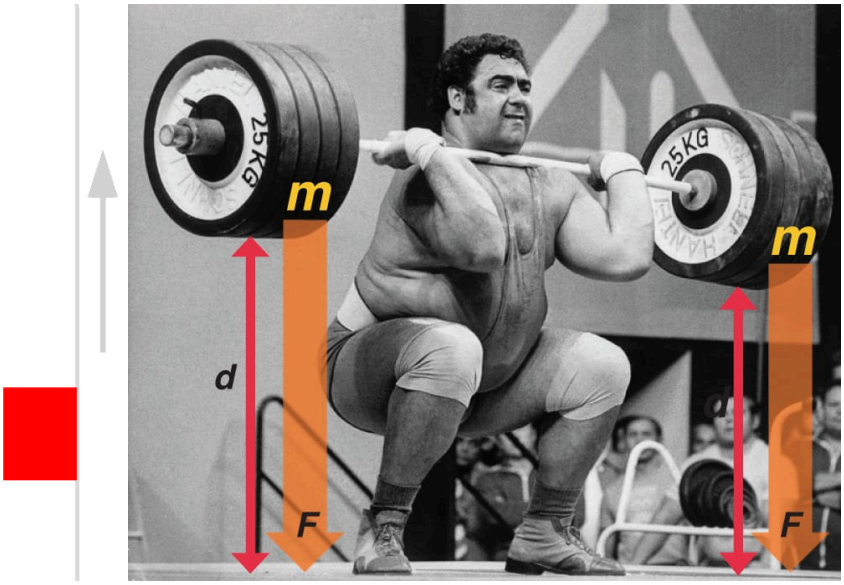


Figure 7.4.1: One form of energy is mechanical work, the energy required to move an object of mass m through distance d when opposed by a force F, i.e., as gravity. (CC BY-SA-NC; anonymous)

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), Equation 7.4.1 can be rewritten to:

$$w = m\,a\,d \tag{7.4.2}$$

with

- w is work
- m is mass

- a is a acceleration, and
- d is distance

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth. Hence for works against gravity (on Earth), a can be set to $g = 9.8\ \ m/s^2$). 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 opposing 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.

Pressure-Volume (PV) Work

To describe this pressure–volume work (PV work), we will use such imaginary oddities as frictionless pistons, which involve no component of resistance, and ideal gases, which have no attractive or repulsive interactions. Imagine, for example, an ideal gas, confined by a frictionless piston, with internal pressure P_{int} and initial volume V_i (Figure 7.4.2). If $P_{ext} = P_{int}$, the system is at equilibrium; the piston does not move, and no work is done. If the external pressure on the piston (P_{ext}) is less than P_{int}, however, then the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings; that is, the final volume (V_f) will be greater than V_i. If $P_{ext} > P_{int}$, then the gas will be compressed, and the surroundings will perform work on the system.

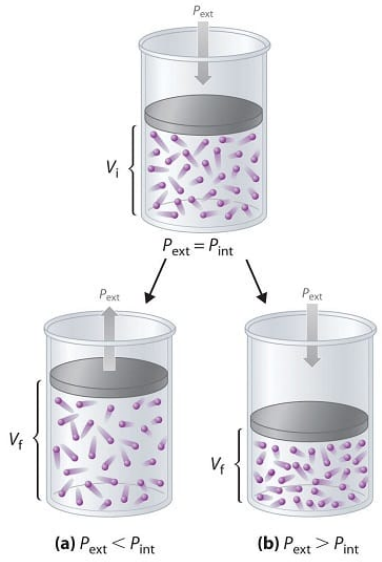


Figure 7.4.2: PV Work demonstrated with a frictionless piston. (a) if the external pressure is less than P_{int}, the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume (V_f) will be greater than V_i. (b) Alternatively, if the external pressure is greater than P_{int}, the gas will be compressed, and the surroundings will perform work on the system.

If the piston has cross-sectional area A, the external pressure exerted by the piston is, by definition, the force per unit area:

$$P_{ext} = \frac{F}{A} \tag{7.4.3}$$

The volume of any three-dimensional object with parallel sides (such as a cylinder) is the cross-sectional area times the height (V = Ah). Rearranging to give F = P_{ext}A and defining the distance the piston moves (d) as Δh, we can calculate the magnitude of the work performed by the piston by substituting into Equation 7.4.1:

$$w = Fd = P_{ext}A\Delta h \tag{7.4.4}$$

The change in the volume of the cylinder (ΔV) as the piston moves a distance d is ΔV = AΔh, as shown in Figure 7.4.3. The work performed is thus

$$w = P_{ext}\Delta V \tag{7.4.5}$$

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m^2) and volume has units of cubic meters, so

$$w = \left(\frac{F}{A}\right)_{\text{ext}}(\Delta V) = \frac{\text{newton}}{\text{m}^2} \times \text{m}^3 = \text{newton} \cdot \text{m} = \text{joule} \tag{7.4.6}$$

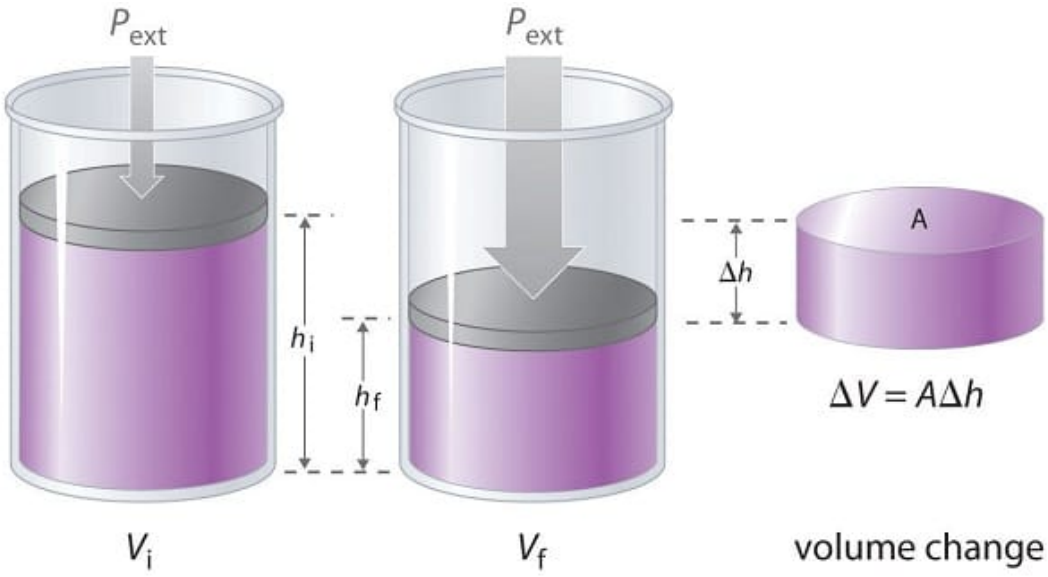


Figure 7.4.3: Work Performed with a change in volume. The change in the volume (ΔV) of the cylinder housing a piston is $\Delta V = A\Delta h$ as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by Equation ???.

If we use atmospheres for P and liters for V, we obtain units of L·atm for work. These units correspond to units of energy, as shown in the different values of the ideal gas constant R:

$$R = \frac{0.08206\ \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = \frac{8.314\ \text{J}}{\text{mol} \cdot \text{K}} \tag{7.4.7}$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J.

Whether work is defined as having a positive sign or a negative sign is a matter of convention. Heat flow is defined from a system to its surroundings as negative; using that same sign convention, we define work done by a system on its surroundings as having a negative sign because it results in a transfer of energy from a system to its surroundings. This is an arbitrary convention and one that is not universally used. Some engineering disciplines are more interested in the work done on the surroundings than in the work done by the system and therefore use the opposite convention. Because $\Delta V > 0$ for an expansion, Equation 7.4.4 must be written with a negative sign to describe PV work done by the system as negative:

$$w = -P_{ext}\Delta V \tag{7.4.8}$$

The work done by a gas expanding against an external pressure is therefore negative, corresponding to work done by a system on its surroundings. Conversely, when a gas is compressed by an external pressure, $\Delta V < 0$ and the work is positive because work is being done on a system by its surroundings.

Note: A Matter of Convention

- Heat flow is defined from the system to its surroundings as **negative**
- Work is defined as by the system on its surroundings as **negative**

Suppose, for example, that the system under study is a mass of steam heated by the combustion of several hundred pounds of coal and enclosed within a cylinder housing a piston attached to the crankshaft of a large steam engine. The gas is not ideal,

and the cylinder is not frictionless. Nonetheless, as steam enters the engine chamber and the expanding gas pushes against the piston, the piston moves, so useful work is performed. In fact, PV work launched the Industrial Revolution of the 19th century and powers the internal combustion engine on which most of us still rely for transportation.

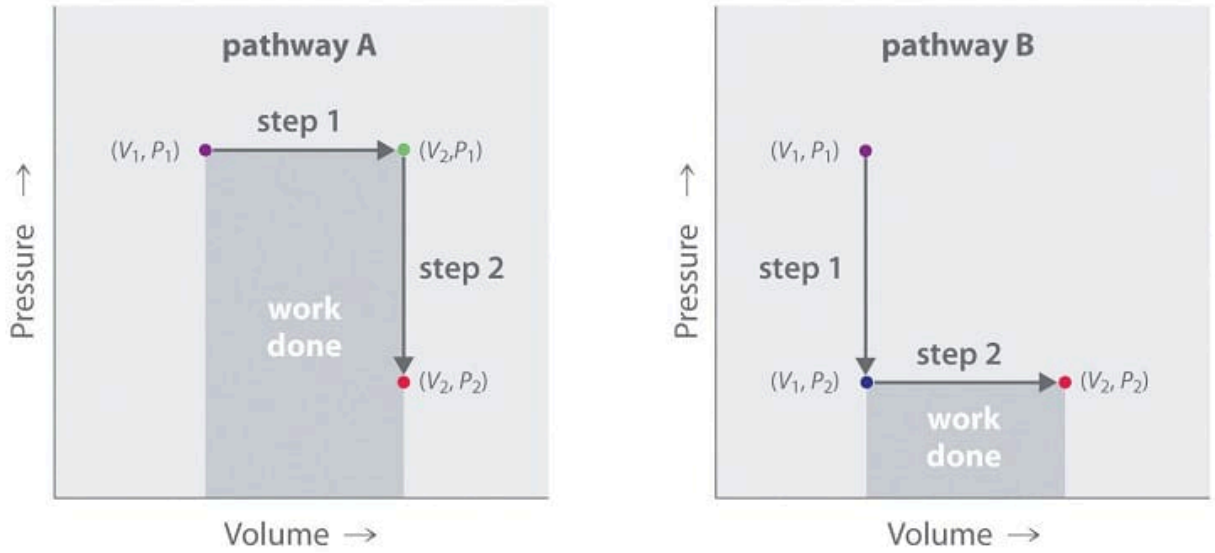


Figure 7.4.4: Work Is Not a State Function. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1). Its pressure is then decreased while the volume remains constant (step 2). Pathway B reverses these steps. Although (V_1, P_1) and (V_2, P_2) are identical in both cases, the amount of work done (shaded area) depends on the pathway taken. (Cc BY-NC-SA; Anonymous by request)

In contrast to internal energy, work is not a state function. We can see this by examining Figure 7.4.4, in which two different, two-step pathways take a gaseous system from an initial state to a final state with corresponding changes in temperature. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1); then its pressure is decreased while the volume remains constant (step 2). In pathway B, the order of the steps is reversed. The temperatures, pressures, and volumes of the initial and final states are identical in both cases, but the amount of work done, indicated by the shaded areas in the figure, is substantially different. As we can see, the amount of work done depends on the pathway taken from (V_1, P_1) to (V_2, P_2), which means that work is **not** a state function.

Note

Internal energy is a state function, whereas work is not.

Example 7.4.1

A small high-performance internal combustion engine has six cylinders with a total nominal displacement (volume) of 2.40 L and a 10:1 compression ratio (meaning that the volume of each cylinder decreases by a factor of 10 when the piston compresses the air–gas mixture inside the cylinder prior to ignition). How much work in joules is done when a gas in one cylinder of the engine expands at constant temperature against an opposing pressure of 40.0 atm during the engine cycle? Assume that the gas is ideal, the piston is frictionless, and no energy is lost as heat.

Given: final volume, compression ratio, and external pressure

Asked for: work done

Strategy:

A. Calculate the final volume of gas in a single cylinder. Then compute the initial volume of gas in a single cylinder from the compression ratio.
B. Use Equation 7.4.5 to calculate the work done in liter-atmospheres. Convert from liter-atmospheres to joules.

Solution:

A To calculate the work done, we need to know the initial and final volumes. The final volume is the volume of one of the six cylinders with the piston all the way down: V_f = 2.40 L/6 = 0.400 L. With a 10:1 compression ratio, the volume of the same cylinder with the piston all the way up is V_i = 0.400 L/10 = 0.0400 L. Work is done by the system on its surroundings, so work is negative.

$$w = -P_{ext}\Delta V = -(40.0 \text{ atm})(0.400 \text{ L} - 0.0400 \text{ L}) = -14.4 \text{ L·atm}$$

Converting from liter-atmospheres to joules,

$$w = -(14.4 \text{ L} \cdot \text{atm})[101.3 \text{ J}/(\text{L} \cdot \text{atm})] = -1.46 \times 10^3 \text{ J} \tag{7.4.9}$$

In the following exercise, you will see that the concept of work is not confined to engines and pistons. It is found in other applications as well.

Exercise 7.4.1

Breathing requires work, even if you are unaware of it. The lung volume of a 70 kg man at rest changed from 2200 mL to 2700 mL when he inhaled, while his lungs maintained a pressure of approximately 1.0 atm. How much work in liter-atmospheres and joules was required to take a single breath? During exercise, his lung volume changed from 2200 mL to 5200 mL on each in-breath. How much additional work in joules did he require to take a breath while exercising?

Answer: −0.500 L·atm, or −50.7 J; −304 J; if he takes a breath every three seconds, this corresponds to 1.4 Calories per minute (1.4 kcal).

Work and 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:

$$Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)} \tag{7.4.10}$$

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 7.4.5). 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)

$$w = -P\Delta V \tag{7.4.11}$$

The negative sign associated with *PV* work done indicates that the system loses energy. 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.

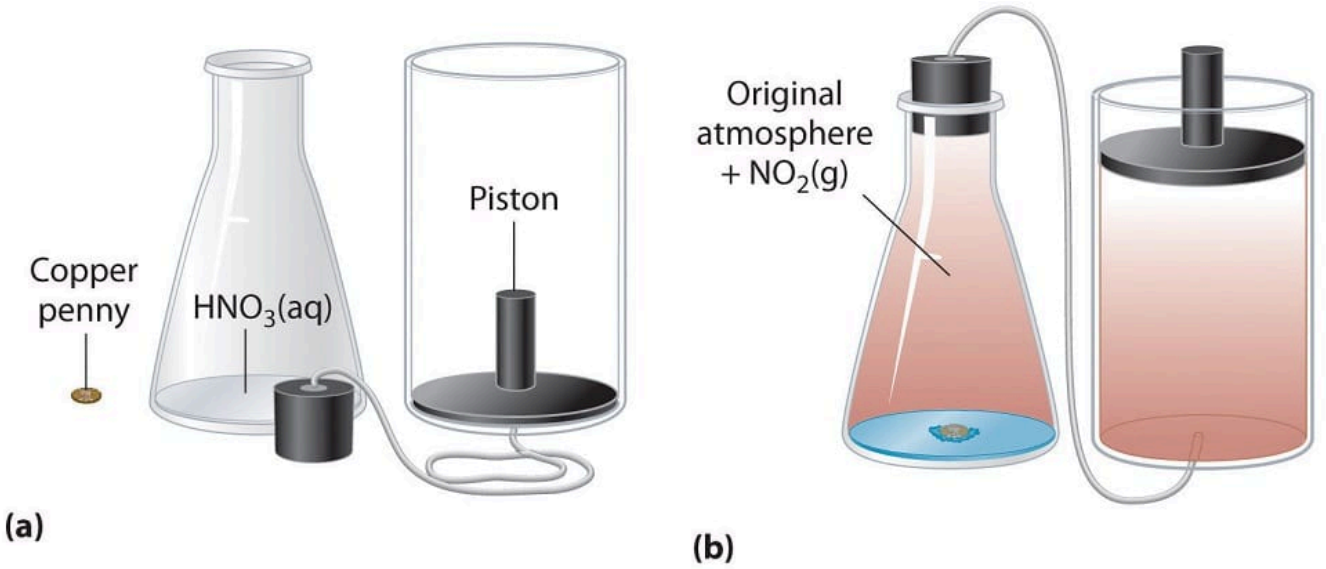


Figure 7.4.5: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.

The symbol U represents the internal energy of a system, which 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*:

$$H = U + PV \tag{7.4.12}$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (i.e., for a given *P*, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta PV = \Delta U + P\Delta V \tag{7.4.13}$$

Substituting $q + w$ for ΔU (Equation 5.2.2) and $-w$ for $P\Delta V$ (Equation 7.4.6), we obtain

$$\Delta H = \Delta U + P\Delta V = q_p + w - w = q_p \tag{7.4.14}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 7.4.9 we see that at constant pressure the change in enthalpy, ΔH of the system, defined as $H_{final} - H_{initial}$, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} = q_p \tag{7.4.15}$$

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.

Note

To find ΔH *for a reaction*, measure q_p.

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.

Exercise 7.4.1

How much work is done by a gas that expands from 2 liters to 5 liters against an external pressure of 750 mmHg?

Answer available at the end of this section.

Exercise 7.4.2

How much work is done by 0.54 moles of a gas that has an initial volume of 8 liters and expands under the following conditions: 30 ^{o}C and 1.3 atm?

Answer available at the end of this section.

Exercise 7.4.3

How much work is done by a gas (p=1.70 atm, V=1.56 L) that expands against an external pressure of 1.80 atm?

Answer available at the end of this section.

Answers

Exercise 7.4.1

$$\begin{aligned} w &= -p\Delta V \\ \Delta V &= V_{final} - V_{initial} \\ &= 5\,\text{L} - 2\,\text{L} \\ &= 3\,\text{L} \end{aligned}$$

Convert 750 mmHg to atm:

$$750\,\text{mmHg}\frac{1\,\text{amt}}{760\,\text{mmHg}} = 0.9868\,\text{atm}.$$

$$w = -p\Delta V = -(0.9868atm)(3Liters) = -2.96\,\text{L atm}.$$

Exercise 7.4.2

First we must find the final volume using the idela gas law:

$$pv = nRT$$

or

$$v = \frac{nRT}{P} = \frac{(0.54moles)(0.082057(Latm)/(molK))(303\,\text{K})}{1.3\,\text{atm}} = 10.33\,\text{L}.$$

$$\Delta V = V_{final} - V_{initial} = 10.3\,\text{L} - 8\,\text{L} = 2.3\,\text{L}$$

$$w = -p\Delta V = -(1.3\,\text{atm})(2.3\,\text{L}) = -3\,\text{L atm}.$$

Exercise 7.4.3

$W = -p\ \Delta V = (-1.80\ \text{atm})\Delta V.$

Given p_1,V_1, and p_2, find V_2:

$p_1V_1 = p_2V_2$ (at constant T and n)

$V_2 = \frac{V_1P_1}{P_2} = \frac{(1.56L)(1.70atm)}{1.80atm} = 1.47\ \text{L}$

Now, $\Delta V = V_2 - V_1 = 1.47L - 1.56L$

$$w = -(1.80\,\text{atm})(1.47\,\text{L} - 1.56\,\text{L}) = 0.162\,\text{L atm}. \tag{7.4.16}$$

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7.5: 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 7.5.1). 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.

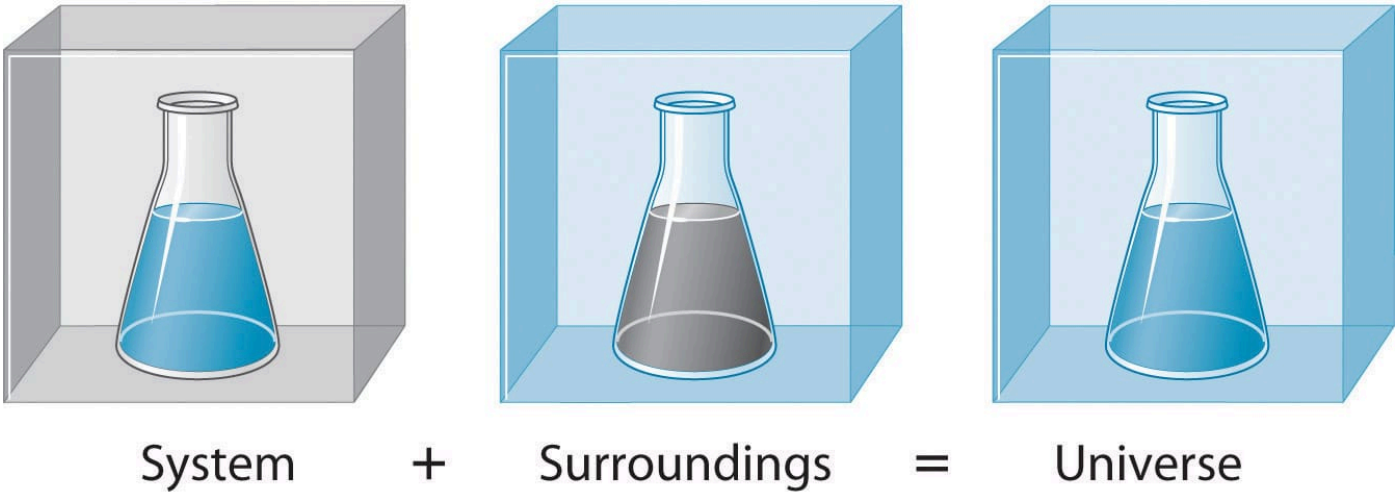


Figure 7.5.1: A System and Its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.

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 7.5.2). 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.

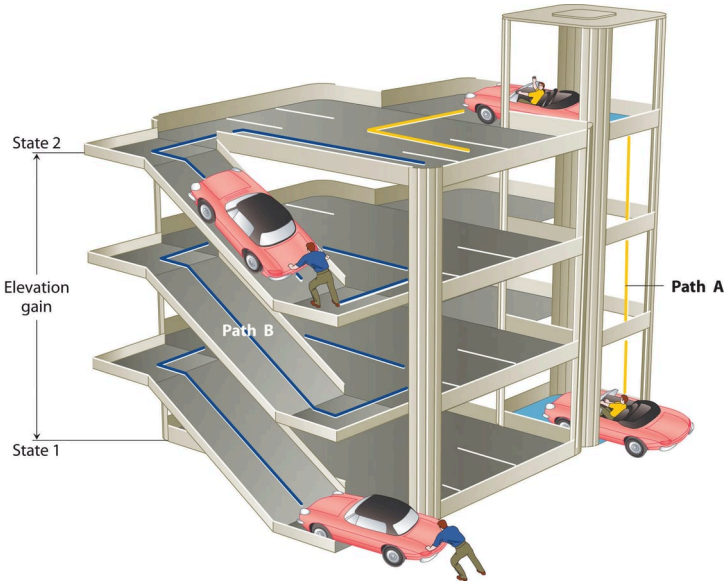


Figure 7.5.2: Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, 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 (see chapter opening image).

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 balanced chemical equation for the reaction is as follows:

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s) \tag{7.5.1}$$

We can also write this chemical equation as

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s) + \text{heat} \tag{7.5.2}$$

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:

$$heat + H_2O_{(s)} \rightarrow H_2O_{(l)} \tag{7.5.3}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

Note: 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 7.5.2 and 7.5.3 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:

$$U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{7.5.4a}$$

$$\Delta U_{sys} = -\Delta U_{surr} \tag{7.5.4b}$$

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.

Note

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):

$$\Delta U_{sys} = q + w \tag{7.5.5}$$

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.

Note

Although q and w are not state functions, their sum (ΔU_{sys}) is independent of the path taken and therefore is a state function.

Example 7.5.1

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 7.5.5.
B. From Equation 7.5.5 calculate w from the values given. Substitute this value into Equation 7.5.5 to calculate ΔU.

Solution

A From Equation 7.5.5, 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 7.5.5,

$$w = -P_{\text{ext}}\Delta V = -8.00\ \text{atm}(0.0500\ \text{L} - 0.400\ \text{L})\left(\frac{101.3\ \text{J}}{\text{L}\cdot\text{atm}}\right) = 284\ \text{J} \tag{7.5.1}$$

Thus

$$\Delta U = q + w = -140\ \text{J} + 284\ \text{J} = 144\ \text{J}$$

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 7.5.1

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: −216 J

Note

By convention, both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

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.

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. 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.

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7.6: Heats of Reactions - ΔU and ΔH

Learning Objectives

- To understand how enthalpy pertains to chemical reactions

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:

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 $7.6.1a$). 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 $7.6.1b$).

Bond breaking **ALWAYS** requires an input of energy; bond making **ALWAYS** releases energy.

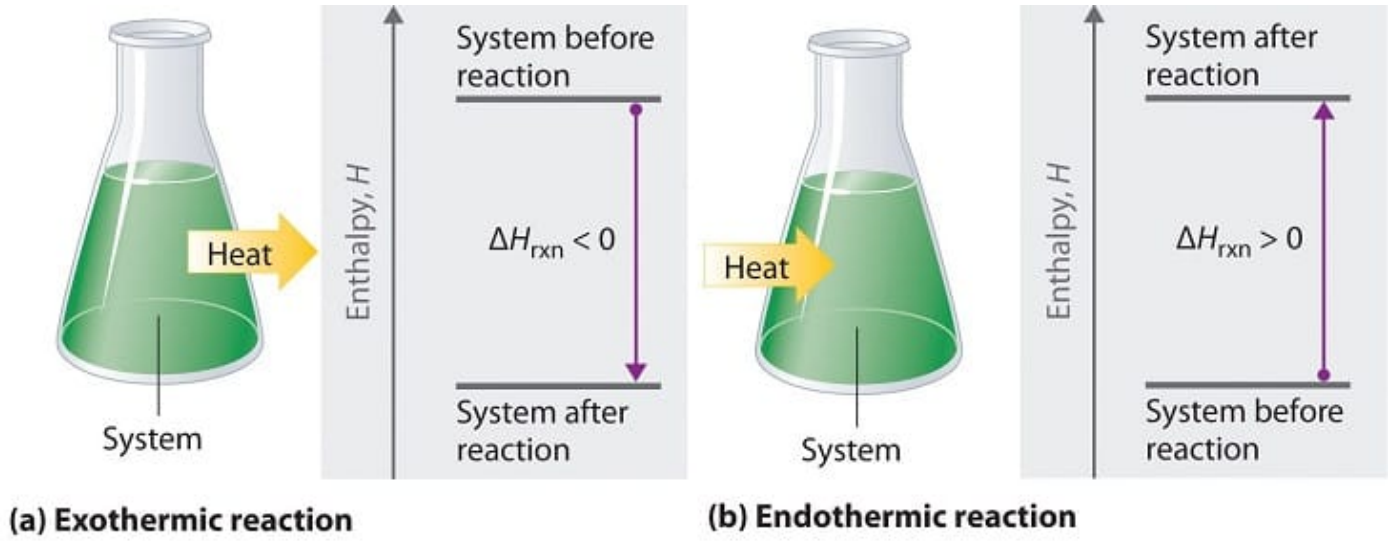


Figure $7.6.1$: The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) 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.

Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

- **Reversing a reaction or a process changes the sign of ΔH.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$\text{heat} + \mathrm{H_2O\,(s)} \longrightarrow \mathrm{H_2O\,(l)} \qquad \Delta\mathrm{H} > 0 \tag{7.6.1}$$

$$\mathrm{H_2O\,(l)} \longrightarrow \mathrm{H_2O\,(s)} + \text{heat} \qquad \Delta\mathrm{H} < 0 \tag{7.6.2}$$

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 7.6.3, 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:

$$2\,\mathrm{Al}\ (\mathrm{s}\ ) + \mathrm{Fe_2O_3}\ (\mathrm{s}\ ) \longrightarrow 2\,\mathrm{Fe\,(s)} + \mathrm{Al_2O_3}\ (\mathrm{s}\ ) + 851.5\ kJ \tag{7.6.3}$$

Thus $\Delta H = -851.5\ kJ/mol$ of $\mathrm{Fe_2O_3}$. 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 7.6.3, it is the value of Δ*H* corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

$$2\,\mathrm{Al\,(s)} + \mathrm{Fe_2O_3\,(s)} \longrightarrow 2\,\mathrm{Fe\,(s)} + \mathrm{Al_2O_3\,(s)} \qquad \Delta H_{rxn} = -851.5\ kJ \tag{7.6.4}$$

If 4 mol of Al and 2 mol of 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:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{7.6.5}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 7.6.1.

7.6.1 Exam

Certain parts of the world, such as southern California and Saudi Arabia, are short of fresh water 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 $\mathrm{H_2O\,(s)} \longrightarrow \mathrm{H_2O\,(l)}$ at 0°C and constant pressure, 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 Δ*H* 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 Δ*H* (+6.01 kJ/mol):

$$moles\ H_2O = 1.00 \times 10^6\ \cancel{metric\ tons}\ H_2O \left(\frac{1000\ \cancel{kg}}{1\ \cancel{metric\ ton}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right)$$

$$= 5.55 \times 10^{10}\ mol H_2O$$

Solution B

he energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55\times10^{10}\ \cancel{mol\ H_2O}\right)=3.34\times10^{11}\ kJ$$

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 in the table below.

Possible sources of the approximately 3.34 × 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

7.6.1Exerc

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.

Types of Enthalpies of Reactions

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, Hess's law 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}) is 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}) is the enthalpy change that accompanies 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}) is 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}) is the change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent.

Table 7.6.1: 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

Substance	ΔH_{vap} (kJ/mol)	ΔH_{fus} (kJ/mol)
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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Enthalpy of Reaction: https://youtu.be/z2KUaIEF9qI

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** (ΔH) can be measured. A negative ΔH means that heat flows from a system to its surroundings; a positive ΔH means that heat flows into a system from its surroundings. 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

- 273 kJ

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7.7: Indirect Determination of ΔH - 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.

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 7.7.1 can be viewed as occurring in three distinct steps with known ΔH values. As shown in Figure 7.7.1:

1. The first reaction produces 1 mol of solid aluminum oxide ($\mathrm{Al_2O_3}$) and 2 mol of liquid iron at its melting point of 1758°C (Equation 7.7.1a); the enthalpy change for this reaction is –732.5 kJ/mol of $\mathrm{Fe_2O_3}$.
2. The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (Equation 7.7.1b); the enthalpy change for this reaction is –13.8 kJ/mol of Fe (–27.6 kJ per 2 mol Fe).
3. In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (Equation 7.7.1c); 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 7.7.1, 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 Equations 7.7.1a-7.7.1c} gives the overall reaction, shown Equation 7.7.1d:

$$\begin{array}{rcll} 2Al\,(s,\ 25^oC) + Fe_2O_3\,(s,\ 25^oC) & \rightarrow & 2Fe\,(l,\ 1758^oC) + Al_2O_3\,(s,\ 1758^oC) & \Delta H = -732.5\ kJ \quad (reaction\,a) \\ 2Fe\,(l,\ 1758^oC) & \rightarrow & 2Fe\,(s,\ 1758^oC) & \Delta H = -\ 27.6\ kJ \quad (reaction\,b) \\ 2Fe\,(s,\ 1758^oC) + 2Al\,(s,\ 1758^oC) & \rightarrow & 2Fe\,(s,\ 25^oC) + 2Al\,(s,\ 25^oC) & \Delta H = -\ 91.0\ kJ \quad (reaction\,c) \\ 2Al\,(s,\ 25^oC) + Fe_2O_3\,(s,\ 25^oC) & \rightarrow & 2Al\,(s,\ 25^oC) + 2Fe_2O_3\,(s,\ 25^oC) & \Delta H = -852.2\ kJ \quad (total\ reaction\,d) \end{array} \tag{7.7.1}$$

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 7.7.1.

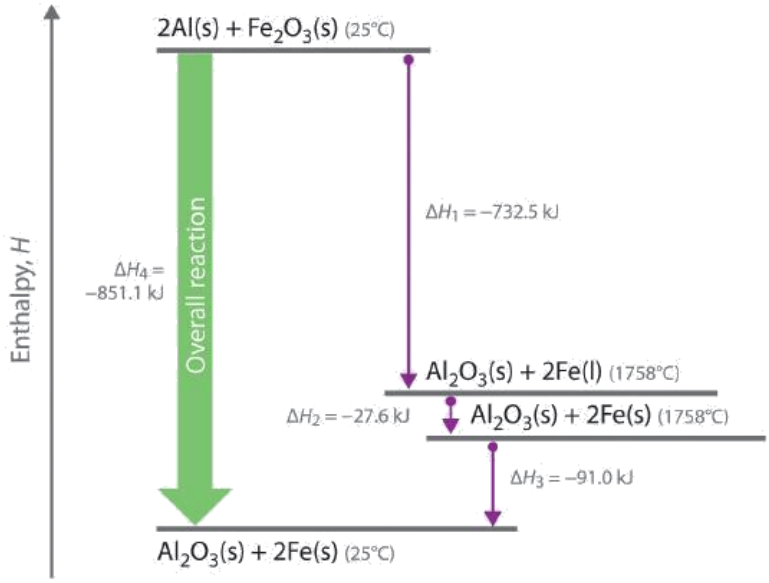


Figure 7.7.1: Energy Changes Accompanying the Thermite Reaction. Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical 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 7.7.1 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 7.7.1), 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 7.7.1). 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 7.7.1.
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 7.7.1

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

$$2\,C\,(s) + O_2\,(g) \longrightarrow 2\,CO\,(g) \qquad \Delta H = -221.0\ kJ \qquad \text{(reaction 1)}$$

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H = -393.5\ kJ \qquad \text{(reaction 2)}$$

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:

$$\mathrm{CO\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(g)} \qquad \Delta H_{rxn} = ? \qquad \text{(reaction 3)}$$

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 reaction 2 and a product in Equation reaction 1, we can reverse reaction 1 to give

$$2CO\,(g) \rightarrow 2C\,(s) + O_2\,(g) \qquad \Delta H = +221.0\ kJ$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use reaction 2, as written because its product, CO_2, is the product we want in reaction 3,:

$$\mathrm{C\,(s) + O_2\,(g) \longrightarrow CO_2\,(s)} \qquad \Delta H = -393.5\ kJ \qquad (7.7.2)$$

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:

$$\mathrm{2\,C\,(s) + 2\,O_2\,(g) \longrightarrow 2\,CO_2\,(s)} \qquad \Delta H = -787.0\ kJ \qquad (7.7.3)$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{array}{rcrcrcrcl} 2CO\,(g) & \rightarrow & \cancel{2C\,(s)} + \cancel{O_2\,(g)} & \Delta H & = & -\Delta H_1 & = & +221.0\ kJ \\ \cancel{2C\,(s)} + \cancel{2}\,O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H & = & -\Delta 2H_2 & = & -787.0\ kJ \\ 2CO\,(g) + O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H & = & -566.0\ kJ & & \end{array} \qquad (7.7.4)$$

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:

$$CO\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = -283.0\ kJ$$

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:

$$\begin{array}{lrcrcrcrcl} (A) & 2C\,(s) + O_2\,(g) & \rightarrow & \cancel{2CO\,(g)} & \Delta H_A & = & \Delta H_1 & = & +221.0\ kJ \\ (B) & \cancel{2CO\,(g)} + O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H_B & & & = & ? \\ (C) & 2C\,(s) + 2O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H & = 2\Delta H_2 & = 2 \times (-393.5\ kJ) & = -787.0\ kJ & \end{array} \qquad (7.7.5)$$

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 7.7.1

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.

Summary

Hess's law is that 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}.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 7.7.1

–136.3 kJ/mol of C_2H_4

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7.8: Standard 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

$$\Delta H_{rxn} = \Delta H_f \tag{7.8.1}$$

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 7.8.1). Therefore, $\mathrm{O_2\,(g)}$, $\mathrm{H_2\,(g)}$, and graphite have ΔH_f^o values of zero.



Figure 7.8.1: 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:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H_f^o = -1273.3\ kJ \tag{7.8.2}$$

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 7.8.2 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 7.8.1: 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 7.8.1

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

$$aA + bB \rightarrow cC + dD \tag{7.8.3}$$

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:

$$\Delta H_{rxn}^o = \underbrace{\left[c\Delta H_f^o(C) + d\Delta H_f^o(D)\right]}_{\text{products}} - \underbrace{\left[a\Delta H_f^o(A) + b\Delta H_f^o(B)\right]}_{\text{reactants}} \tag{7.8.4}$$

More generally, we can write

$$\Delta H_{rxn}^o = \sum m\Delta H_f^o(products) - \sum n\Delta H_f^o(reactants) \tag{7.8.5}$$

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 7.8.5 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:

$$\mathrm{C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)} \tag{7.8.6}$$

Using Equation 7.8.5, we write

$$\Delta H_f^o = \left\{6\Delta H_f^o\left[CO_2(g)\right] + 6\Delta H_f^o\left[H_2O(g)\right]\right\} - \left\{\Delta H_f^o\left[C_6H_{12}O_6(s)\right] + 6\Delta H_f^o\left[O_2(g)\right]\right\} \tag{7.8.7}$$

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 7.8.7 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\Delta H^o_{comb} = [6\,(-393.5\ kJ/mol) + 6\,(-285.8\ kJ/mol)] - [-1273.3 + 6\,(0\ kJ\ mol)] \tag{7.8.8}$$

$$= -2802.5\ kJ/mol \tag{7.8.9}$$

As illustrated in Figure 7.8.2, we can use Equation 7.8.8 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

$$\begin{aligned}
\Delta H^o_1 &= \Delta H^o_f\,[glucose\,(s)] \\
&= -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right) \\
&= +1273.3\ kJ \\
\Delta H^o_2 &= 6\Delta H^o_f\,[O_2\,(g)] \\
&= 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right) \\
&= 0\ kJ
\end{aligned} \tag{7.8.10}$$

Recall that when we reverse a reaction, we must also reverse the **sign** of the accompanying enthalpy change (Equation 7.8.4 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.

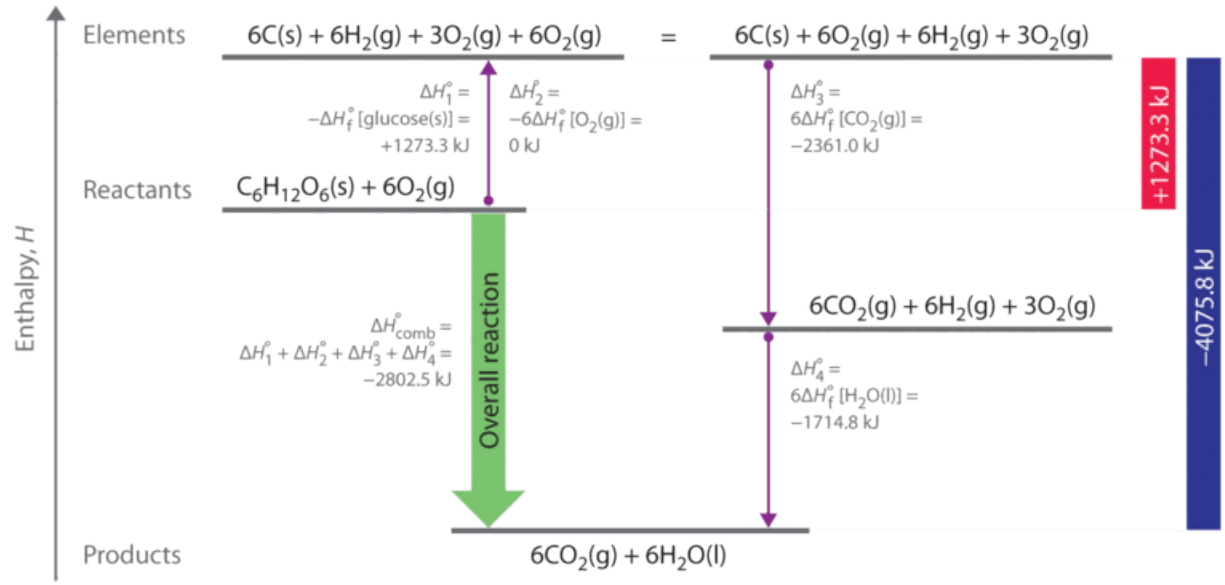


Figure 7.8.1: A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the 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 7.8.2) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes (from Table T1) are

$$\Delta H_3^o = \Delta H_f^o\left[CO_2\left(g\right)\right] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ$$
$$\Delta H_4^o = 6\Delta H_f^o\left[H_2O\left(l\right)\right] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ \tag{7.8.11}$$

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):

$$\Delta H_{comb}^o = +1273.3\ kJ + (-4075.8\ kJ) = -2802.5\ kJ \tag{7.8.12}$$

This is the same result we obtained using the "products minus reactants" rule (Equation 7.8.5) and ΔH^0_f values. The two results must be the same because Equation 7.8.12 is just a more compact way of describing the thermochemical cycle shown in Figure 7.8.1.

Example 7.8.2: 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 7.8.5 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 7.8.8 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 7.8.5 ("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 7.8.8, \(ΔH^o_f\) 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 7.8.2: 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):

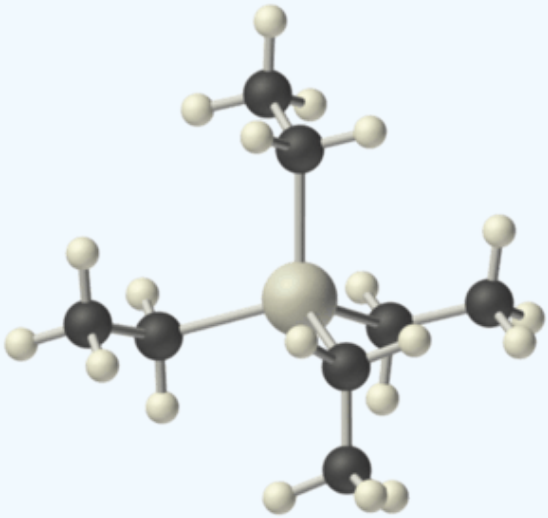
$$\mathrm{CO\ (\ g\ ) + H_2O\ (g\ ) \longrightarrow CO_2\,(g) + H_2\ (\ g\ )}$$

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 7.8.3.

Example 7.8.3: 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 7.8.5 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 7.8.5 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 7.8.3

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

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

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 $7.8.1$**: 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 7.8.1

$$\mathrm{Na(s) + \tfrac{1}{2}\,Cl_2(g) \rightarrow NaCl(s)}$$

$$\mathrm{H_2(g) + \tfrac{1}{8}\,S_8(s) + 2\,O_2(\ g) \rightarrow H_2\ SO_4(\ l)}$$

$$\mathrm{2\,C(s) + O_2(g) + 2\,H_2(g) \longrightarrow CH_3CO_2H(l)}$$

Exercise 7.8.2**: Water–gas shift reaction**

–41.2 kJ/mol

Exercise 7.8.3

–1181 kJ/mol

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7.9: Fuels as Sources of Energy

Learning Objectives

- To use thermochemical concepts to solve environmental issues.

Our contemporary society requires the constant expenditure of huge amounts of energy to heat our homes, provide telephone and cable service, transport us from one location to another, provide light when it is dark outside, and run the machinery that manufactures material goods. The United States alone consumes almost 10^6 kJ per person per day, which is about 100 times the normal required energy content of the human diet. This figure is about 30% of the world's total energy usage, although only about 5% of the total population of the world lives in the United States. In contrast, the average energy consumption elsewhere in the world is about 10^5 kJ per person per day, although actual values vary widely depending on a country's level of industrialization. In this section, we describe various sources of energy and their impact on the environment.

Fuels

According to the law of conservation of energy, energy can never actually be "consumed"; it can only be changed from one form to another. What *is* consumed on a huge scale, however, are resources that can be readily converted to a form of energy that is useful for doing work. Energy that is not used to perform work is either stored as potential energy for future use or transferred to the surroundings as heat.

A major reason for the huge consumption of energy by our society is the low *efficiency* of most machines in transforming stored energy into work. Efficiency can be defined as the ratio of useful work accomplished to energy expended. Automobiles, for example, are only about 20% efficient in converting the energy stored in gasoline to mechanical work; the rest of the energy is released as heat, either emitted in the exhaust or produced by friction in bearings and tires. The production of electricity by coal- or oil-powered steam turbines (Figure 7.9.1) is can be more than 50% efficient.

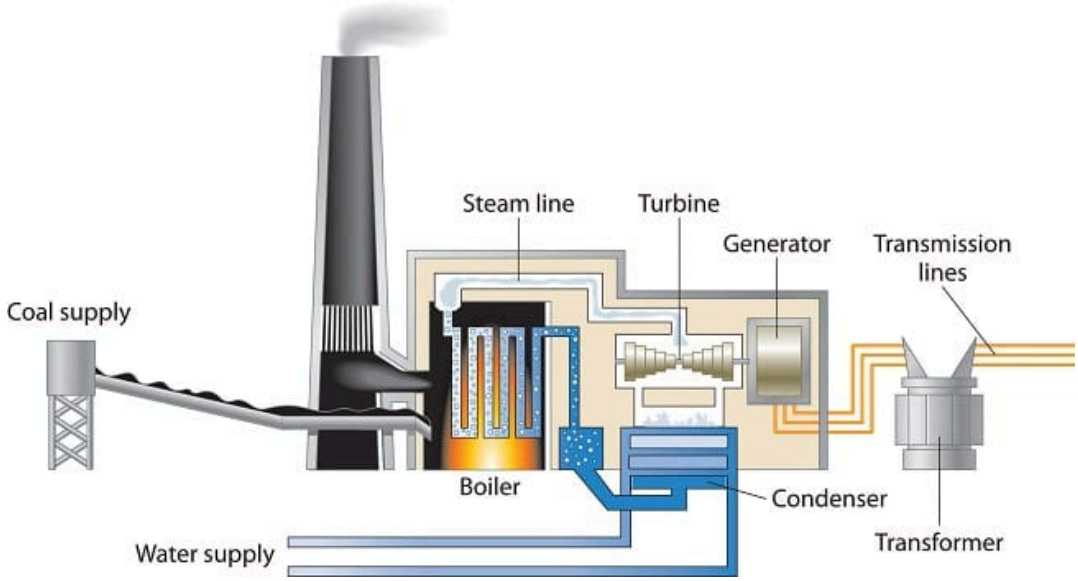


Figure 7.9.1: Electricity from Coal. A coal-powered electric power plant uses the combustion of coal to produce steam, which drives a turbine to produce electricity.

In general, it is more efficient to use primary sources of energy directly (such as natural gas or oil) than to transform them to a secondary source such as electricity prior to their use. For example, if a furnace is well maintained, heating a house with natural gas is about 70% efficient. In contrast, burning the natural gas in a remote power plant, converting it to electricity, transmitting it long distances through wires, and heating the house by electric baseboard heaters have an overall efficiency of less than 35%.

The total expenditure of energy in the world each year is about 3×10^{17} kJ. 80% of this energy is provided by the combustion of fossil fuels: oil, coal, and natural gas (the sources of the energy consumed in the United States in 2019 are shown in Figure 7.9.2). Natural gas and petroleum are the preferred fuels because many of the products derived from them are gases or liquids that are readily transported, stored, and burned. Natural gas and petroleum are derived from the remains of marine creatures that died hundreds of millions of years ago and were buried beneath layers of sediment. As the sediment turned to rock, the tremendous heat and pressure inside Earth transformed the organic components of the buried sea creatures to petroleum and natural gas.

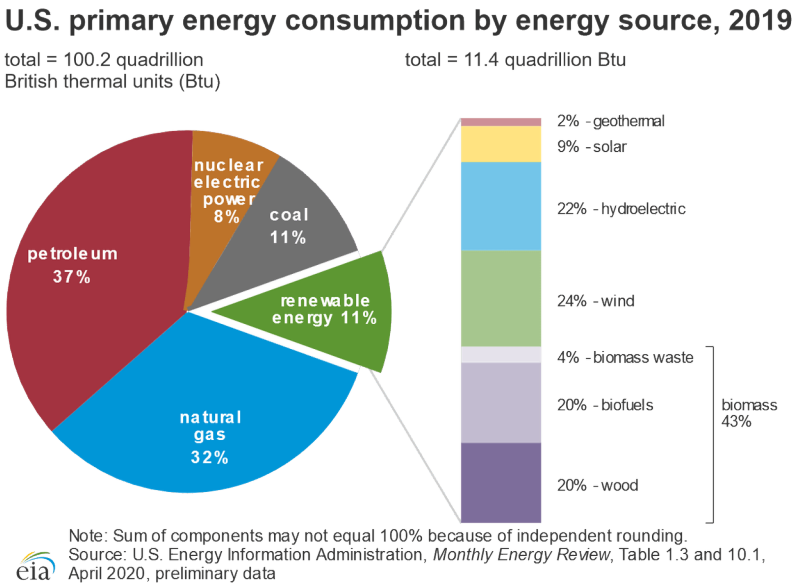


Figure 7.9.2: Energy Consumption in the United States by Source, 2014. More than 75% of the total energy expended is provided by the combustion of fossil fuels, such as oil, coal, and natural gas. (Public Domain; U.S. Energy Information Administration)

Coal

Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. Because plants contain large amounts of *cellulose*, derived from linked glucose units, the structure of coal is more complex than that of petroleum (Figure 7.9.3). In particular, coal contains a large number of oxygen atoms that link parts of the structure together, in addition to the basic framework of carbon–carbon bonds. It is impossible to draw a single structure for coal; however, because of the prevalence of rings of carbon atoms (due to the original high cellulose content), coal is more similar to an aromatic hydrocarbon than an aliphatic one.

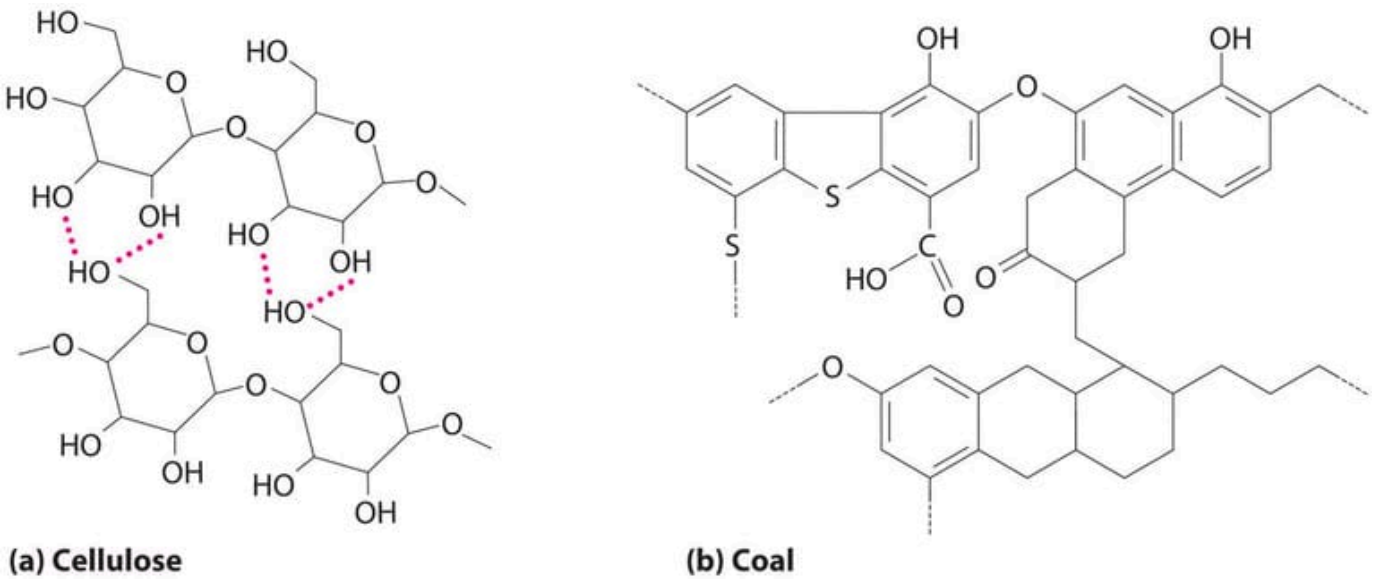


Figure 7.9.3: The Structures of Cellulose and Coal. (a) Cellulose consists of long chains of cyclic glucose molecules linked by hydrogen bonds. (b) When cellulose is subjected to high pressures and temperatures for long periods of time, water is eliminated, and bonds are formed between the rings, eventually producing coal. This drawing shows some of the common structural features of coal; note the presence of many different kinds of ring structures.

Table 7.9.1: Properties of Different Types of Coal

Type	% Carbon	Hydrogen:Carbon Mole Ratio	% Oxygen	% Sulfur	Heat Content	US Deposits
anthracite	92	0.5	3	1	high	Pennsylvania, New York
bituminous	80	0.6	8	5	medium	Appalachia, Midwest, Utah
subbituminous	77	0.9	16	1	medium	Rocky Mountains
lignite	71	1.0	23	1	low	Montana

There are four distinct classes of coal (Table 7.9.1); their hydrogen and oxygen contents depend on the length of time the coal has been buried and the pressures and temperatures to which it has been subjected. Lignite, with a hydrogen:carbon ratio of about 1.0 and a high oxygen content, has the lowest ΔH_{comb}. Anthracite, in contrast, with a hydrogen:carbon ratio of about 0.5 and the lowest oxygen content, has the highest ΔH_{comb} and is the highest grade of coal. The most abundant form in the United States is bituminous coal, which has a high sulfur content because of the presence of small particles of pyrite (FeS_2). The combustion of coal releases the sulfur in FeS_2 as SO_2, which is a major contributor to acid rain. Table 7.9.2 compares the ΔH_{comb} per gram of oil, natural gas, and coal with those of selected organic compounds.

Table 7.9.2: Enthalpies of Combustion of Common Fuels and Selected Organic Compounds

Fuel	ΔH_{comb} (kJ/g)
dry wood	−15
peat	−20.8
bituminous coal	−28.3
charcoal	−35
kerosene	−37
C_6H_6 (benzene)	−41.8
crude oil	−43
natural gas	−50
C_2H_2 (acetylene)	−50.0

Fuel	ΔH_{comb} (kJ/g)
CH_4 (methane)	–55.5
gasoline	–84
hydrogen	–143

Peat, a precursor to coal, is the partially decayed remains of plants that grow in swampy areas. It is removed from the ground in the form of soggy bricks of mud that will not burn until they have been dried. Even though peat is a smoky, poor-burning fuel that gives off relatively little heat, humans have burned it since ancient times (Figure 7.9.4). If a peat bog were buried under many layers of sediment for a few million years, the peat could eventually be compressed and heated enough to become lignite, the lowest grade of coal; given enough time and heat, lignite would eventually become anthracite, a much better fuel.



Figure 7.9.4: A Peat Bog. Peat is a smoky fuel that burns poorly and produces little heat, but it has been used as a fuel since ancient times.

Converting Coal to Gaseous and Liquid Fuels

Oil and natural gas resources are limited. Current estimates suggest that the known reserves of petroleum will be exhausted in about 60 years, and supplies of natural gas are estimated to run out in about 120 years. Coal, on the other hand, is relatively abundant, making up more than 90% of the world's fossil fuel reserves. As a solid, coal is much more difficult to mine and ship than petroleum (a liquid) or natural gas. Consequently, more than 75% of the coal produced each year is simply burned in power plants to produce electricity. A great deal of current research focuses on developing methods to convert coal to gaseous fuels (*coal* gasification) or liquid fuels (coal liquefaction). In the most common approach to coal gasification, coal reacts with steam to produce a mixture of CO and H2 known as synthesis gas, or syngas:Because coal is 70%–90% carbon by mass, it is approximated as C in Equation 7.9.1.

$$\mathrm{C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \quad \Delta H = 131\ kJ} \tag{7.9.1}$$

Converting coal to syngas removes any sulfur present and produces a clean-burning mixture of gases.

Syngas is also used as a reactant to produce methane and methanol. A promising approach is to convert coal directly to methane through a series of reactions:

$$\begin{array}{llll} 2\mathrm{C(s) + 2H_2O(g) \rightarrow \cancel{2CO(g)} + \cancel{2H_2(g)}} & \Delta H_1 = 262\ \mathrm{kJ} & \cancel{\mathrm{CO(g)}} + \cancel{\mathrm{H_2O(g)}} \rightarrow \mathrm{CO_2(g)} + \cancel{\mathrm{H_2(g)}} & \Delta H_2 = -41\ \mathrm{kJ} \\ \cancel{\mathrm{CO(g)}} + \cancel{3\mathrm{H_2(g)}} \rightarrow \mathrm{CH_4(g)} + \cancel{\mathrm{H_2O(g)}} & \Delta H_3 = -206\ \mathrm{kJ} & \mathrm{Overall:\ 2C(s) + 2H_2O(g) \rightarrow CH_4(g) + CO_2(g)} & \Delta H_{comb} = 15\ \mathrm{kJ} \end{array}$$

Burning a small amount of coal or methane provides the energy consumed by these reactions. Unfortunately, methane produced by this process is currently significantly more expensive than natural gas. As supplies of natural gas become depleted, however,

this coal-based process may well become competitive in cost.



Measuring crude oil. The standard industrial unit of measure for crude oil is the 42 gal barrel.

Similarly, the techniques available for converting coal to liquid fuels are not yet economically competitive with the production of liquid fuels from petroleum. Current approaches to coal liquefaction use a catalyst to break the complex network structure of coal into more manageable fragments. The products are then treated with hydrogen (from syngas or other sources) under high pressure to produce a liquid more like petroleum. Subsequent distillation, cracking, and reforming can be used to create products similar to those obtained from petroleum. The total yield of liquid fuels is about 5.5 bbl of crude liquid per ton of coal (1 bbl is 42 gal or 160 L). Although the economics of coal liquefaction are currently even less attractive than for coal gasification, liquid fuels based on coal are likely to become economically competitive as supplies of petroleum are consumed.

Example 7.9.1

If bituminous coal is converted to methane by the process in Equation 7.9.1, what is the ratio of the ΔH_{comb} of the methane produced to the enthalpy of the coal consumed to produce the methane? (Note that 1 mol of CH_4 is produced for every 2 mol of carbon in coal.)

Given: chemical reaction and ΔH_{comb} (Table 7.9.2)

Asked for: ratio of ΔH_{comb} of methane produced to coal consumed

Strategy:

A Write a balanced chemical equation for the conversion of coal to methane. Referring to Table 7.9.2, calculate the ΔH_{comb} of methane and carbon.

B Calculate the ratio of the energy released by combustion of the methane to the energy released by combustion of the carbon.

Solution:

A The balanced chemical equation for the conversion of coal to methane is as follows:

$$2\,C\,(s) + 2\,H_2O\,(g) \longrightarrow CH_4\,(g) + CO_2\,(g)$$

Thus 1 mol of methane is produced for every 2 mol of carbon consumed. The ΔH_{comb} of 1 mol of methane is

$$1\ \text{mol}\ CH_4 \left(\frac{16.043\ g}{1\ \text{mol}\ CH_4}\right)\left(\frac{-55.5\ \text{kJ}}{g}\right) = -890\ \text{kJ}$$

The ΔH_{comb} of 2 mol of carbon (as coal) is

$$2\ \text{mol}\ C \left(\frac{12.011\ g}{1\ \text{mol}\ C}\right)\left(\frac{-28.3\ \text{kJ}}{g}\right) = -680\ \text{kJ}$$

B The ratio of the energy released from the combustion of methane to the energy released from the combustion of carbon is

$$\frac{-890\ \text{kJ}}{-680\ \text{kJ}} = 1.31$$

The energy released from the combustion of the product (methane) is 131% of that of the reactant (coal). The fuel value of coal is actually increased by the process!

How is this possible when the law of conservation of energy states that energy cannot be created? The reaction consumes 2 mol of water ($\Delta H_f^\circ = -285.8\ \text{kJ/mol}$) but produces only 1 mol of CO2 ($\Delta H_f^\circ = -393.5\ \text{kJ/mol}$). Part of the difference in potential energy between the two (approximately 180 kJ/mol) is stored in CH4 and can be released during combustion.

Exercise 7.9.1

Using the data in Table 7.9.2, calculate the mass of hydrogen necessary to provide as much energy during combustion as 1 bbl of crude oil (density approximately 0.75 g/mL).

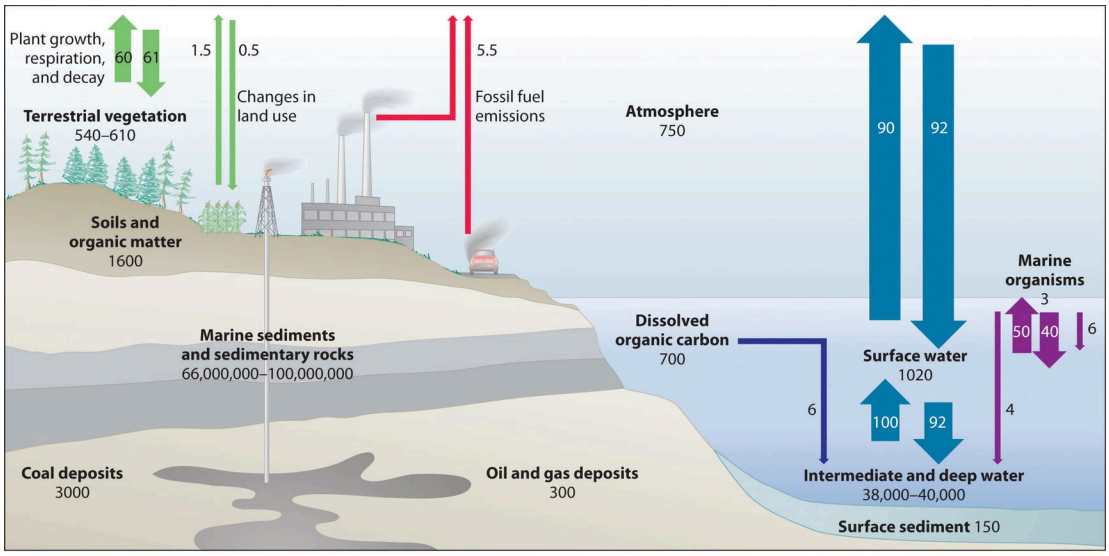
Answer available at the end of this section.

The Carbon Cycle and the Greenhouse Effect

Even if carbon-based fuels could be burned with 100% efficiency, producing only CO_2(g) and H_2O(g), doing so could still potentially damage the environment when carried out on the vast scale required by an industrial society. The amount of CO_2 released is so large and is increasing so rapidly that it is apparently overwhelming the natural ability of the planet to remove CO_2 from the atmosphere. In turn, the elevated levels of CO_2 are thought to be affecting the temperature of the planet through a mechanism known as the greenhouse effect. As you will see, there is little doubt that atmospheric CO_2 levels are increasing, and the major reason for this increase is the combustion of fossil fuels. There is substantially less agreement, however, on whether the increased CO_2 levels are responsible for a significant increase in temperature.

The Global Carbon Cycle

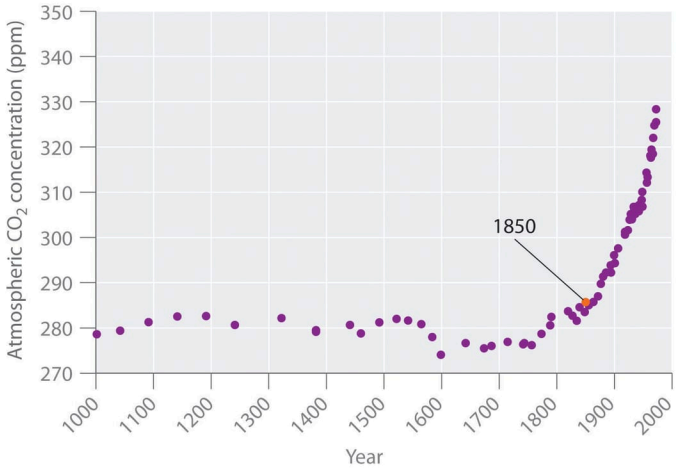
Figure 7.9.5 illustrates the global carbon cycle, the distribution and flow of carbon on Earth. Normally, the fate of atmospheric CO_2 is to either (1) dissolve in the oceans and eventually precipitate as carbonate rocks or (2) be taken up by plants. The rate of uptake of CO_2 by the ocean is limited by its surface area and the rate at which gases dissolve, which are approximately constant. The rate of uptake of CO_2 by plants, representing about 60 billion metric tons of carbon per year, partly depends on how much of Earth's surface is covered by vegetation. Unfortunately, the rapid deforestation for agriculture is reducing the overall amount of vegetation, and about 60 billion metric tons of carbon are released annually as CO_2 from animal respiration and plant decay. The amount of carbon released as CO_2 every year by fossil fuel combustion is estimated to be about 5.5 billion metric tons. The net result is a system that is slightly out of balance, experiencing a slow but steady increase in atmospheric CO_2 levels (Figure 7.9.6). As a result, average CO_2 levels have increased by about 30% since 1850.



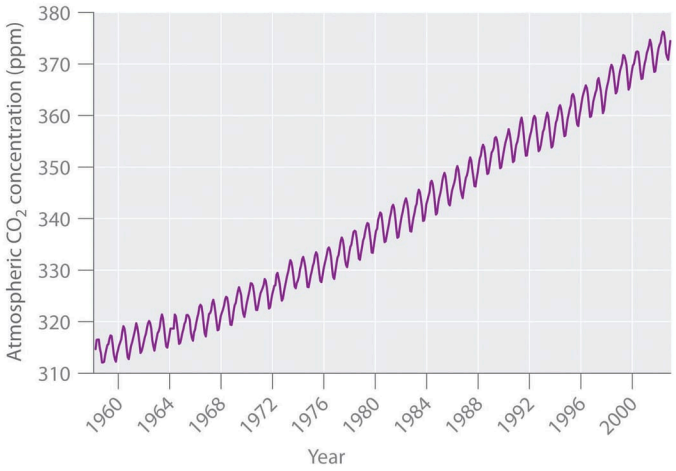
Volumes and exchanges in billions of metric tons

Figure 7.9.5: The Global Carbon Cycle

Most of Earth's carbon is found in the crust, where it is stored as calcium and magnesium carbonate in sedimentary rocks. The oceans also contain a large reservoir of carbon, primarily as the bicarbonate ion (HCO_3^-). Green plants consume about 60 billion metric tons of carbon per year as CO_2 during photosynthesis, and about the same amount of carbon is released as CO_2 annually from animal and plant respiration and decay. The combustion of fossil fuels releases about 5.5 billion metric tons of carbon per year as CO_2.



(a) Records from Antarctic ice cores (1006–1969)



(b) Records from monthly air samples, Mauna Loa Observatory, Hawaii (1958–2002)

Figure 7.9.6: Changes in Atmospheric CO_2 Levels. (a) Average worldwide CO_2 levels have increased by about 30% since 1850. (b) Atmospheric CO_2 concentrations measured at Mauna Loa in Hawaii show seasonal variations caused by the removal of CO_2 from the atmosphere by green plants during the growing season along with a general increase in CO_2 levels.

The Atmospheric Greenhouse Effect

The increasing levels of atmospheric CO_2 are of concern because CO_2 absorbs thermal energy radiated by the Earth, as do other gases such as water vapor, methane, and chlorofluorocarbons. Collectively, these substances are called greenhouse gases; they mimic the effect of a greenhouse by trapping thermal energy in the Earth's atmosphere, a phenomenon known as the greenhouse effect (Figure 7.9.7).

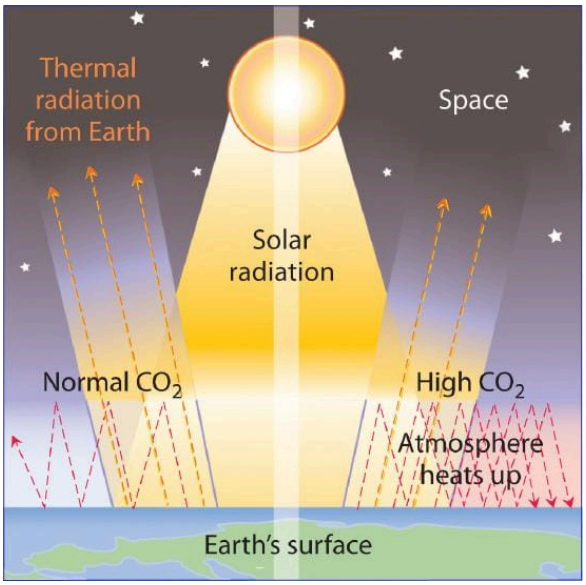


Figure 7.9.7: The Greenhouse Effect. Thermal energy can be trapped in Earth's atmosphere by gases such as CO_2, water vapor, methane, and chlorofluorocarbons before it can be radiated into space—like the effect of a greenhouse. It is not yet clear how large an increase in the temperature of Earth's surface can be attributed to this phenomenon.

Venus is an example of a planet that has a runaway greenhouse effect. The atmosphere of Venus is about 95 times denser than that of Earth and contains about 95% CO_2. Because Venus is closer to the sun, it also receives more solar radiation than Earth does. The result of increased solar radiation and high CO_2 levels is an average surface temperature of about 450°C, which is hot enough to melt lead.

Data such as those in Figure Figure 7.9.6 indicate that atmospheric levels of greenhouse gases have increased dramatically over the past 100 years, and it seems clear that the heavy use of fossil fuels by industry is largely responsible. It is not clear, however, how large an increase in temperature (*global warming*) may result from a continued increase in the levels of these gases. Estimates of the effects of doubling the preindustrial levels of CO_2 range from a 0°C to a 4.5°C increase in the average temperature of Earth's surface, which is currently about 14.4°C. Even small increases, however, could cause major perturbations in our planet's delicately balanced systems. For example, an increase of 5°C in Earth's average surface temperature could cause extensive melting of glaciers and the Antarctic ice cap. It has been suggested that the resulting rise in sea levels could flood highly populated coastal areas, such as New York City, Calcutta, Tokyo, Rio de Janeiro, and Sydney. An analysis conducted in 2009 by leading climate researchers from the US National Oceanic and Atmospheric Administration, Switzerland, and France shows that CO_2 in the atmosphere will remain near peak levels far longer than other greenhouse gases, which dissipate more quickly. The study predicts a rise in sea levels of approximately 3 ft by the year 3000, excluding the rise from melting glaciers and polar ice caps. According to the analysis, southwestern North America, the Mediterranean, and southern Africa are projected to face droughts comparable to that of the Dust Bowl of the 1930s as a result of global climate changes.

The increase in CO_2 levels is only one of many trends that can affect Earth's temperature. In fact, geologic evidence shows that the average temperature of Earth has fluctuated significantly over the past 400,000 years, with a series of glacial periods (during which the temperature was 10°C–15°C *lower* than it is now and large glaciers covered much of the globe) interspersed with relatively short, warm interglacial periods (Figure 7.9.8). Although average temperatures appear to have increased by 0.5°C in the last century, the statistical significance of this increase is open to question, as is the existence of a cause-and-effect relationship between the temperature change and CO_2 levels. Despite the lack of incontrovertible scientific evidence, however, many people believe that we should take steps now to limit CO_2 emissions and explore alternative sources of energy, such as solar energy, geothermal energy from volcanic steam, and nuclear energy, to avoid even the possibility of creating major perturbations in Earth's environment. In 2010, international delegates met in Cancún, Mexico, and agreed on a broad array of measures that would advance climate protection. These included the development of low-carbon technologies, providing a framework to reduce deforestation, and aiding countries in assessing their own vulnerabilities. They avoided, however, contentious issues of assigning emissions reductions commitments.

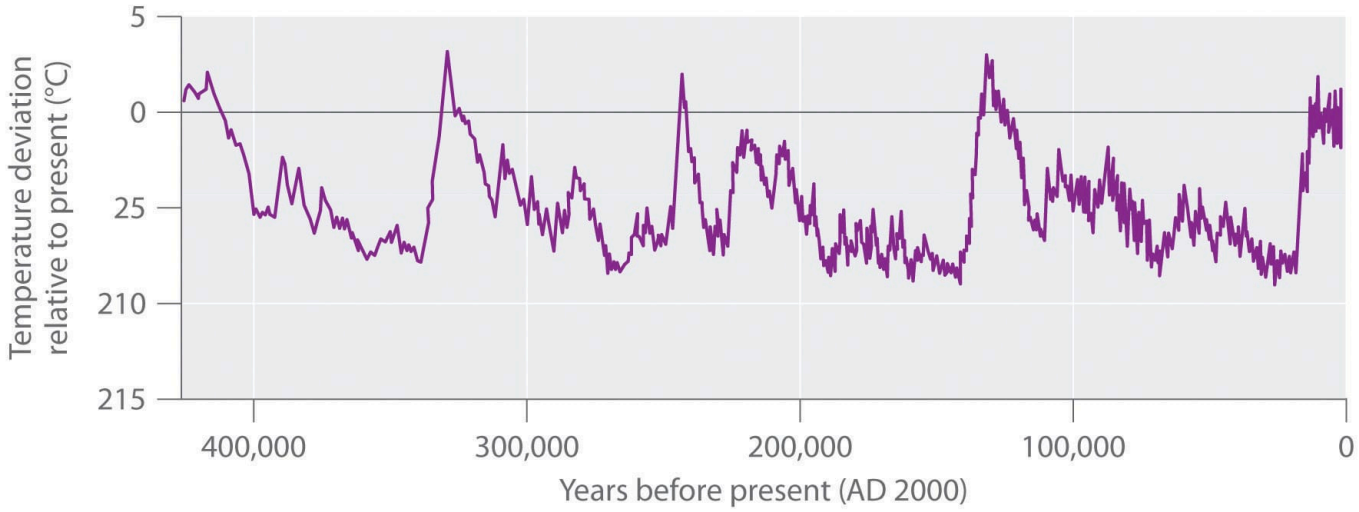


Figure 7.9.8: Average Surface Temperature of Earth over the Past 400,000 Years. The dips correspond to glacial periods, and the peaks correspond to relatively short, warm interglacial periods. Because of these fluctuations, the statistical significance of the 0.5°C increase in average temperatures observed in the last century is open to question.

Example 7.9.2

A student at UCLA decided to fly home to New York for Christmas. The round trip was 4500 air miles, and part of the cost of her ticket went to buy the 100 gal of jet fuel necessary to transport her and her baggage. Assuming that jet fuel is primarily *n*-dodecane ($C_{12}H_{26}$) with a density of 0.75 g/mL, how much energy was expended and how many tons of CO_2 were emitted into the upper atmosphere to get her home and back?

Given: volume and density of reactant in combustion reaction

Asked for: energy expended and mass of CO_2 emitted

Strategy:

A After writing a balanced chemical equation for the reaction, calculate $\Delta H^\circ_{\text{comb}}$

B Determine the number of moles of dodecane in 100 gal by using the density and molar mass of dodecane and the appropriate conversion factors.

C Obtain the amount of energy expended by multiplying $\Delta H^\circ_{\text{comb}}$ by the number of moles of dodecane. Calculate the amount of CO2 emitted in tons by using mole ratios from the balanced chemical equation and the appropriate conversion factors.

Solution

A We first need to write a balanced chemical equation for the reaction:

$$2\,C_{12}H_{26}\,(l) + 37\,O_2\,(g) \longrightarrow 24\,CO_2\,(g) + 26\,H_2O\,(l)$$

We can calculate $\Delta H^\circ_{\text{comb}}$ using the ΔH°_f values corresponding to each substance in the specified phase (phases are not shown for simplicity):

$$\begin{aligned}\Delta H^\circ_{\text{comb}} &= \Sigma m \Delta H^\circ_f(\text{products}) - \Sigma n \Delta H^\circ_f(\text{reactants}) \\ &= [24\Delta H^\circ_f(CO_2) + 26\Delta H^\circ_f(H_2O)] - [37\Delta H^\circ_f(O_2) + 2\Delta H^\circ_f(C_{12}H_{26})] \\ &= [24(-393.5\ \text{kJ/mol}\ CO_2) + 26(-285.8\ \text{kJ/mol}\ H_2O)] \\ &\quad -[37(0\ \text{kJ/mol}\ O_2) + 2(-350.9\ \text{kJ/mol}\ C_{12}H_{26})] \\ &= -16,173.0\ \text{kJ}\end{aligned}$$

According to the balanced chemical equation for the reaction, this value is $\Delta H^\circ_{\text{comb}}$ for the combustion of 2 mol of n-dodecane. So we must divide by 2 to obtain $\Delta H^\circ_{\text{comb}}$ per mole of n-dodecane:

$$\Delta H^\circ_{\text{comb}} = -8,086.5 \text{ kJ/mol } C_{12}H_{26}$$

B The number of moles of dodecane in 100 gal can be calculated as follows, using density, molar mass, and appropriate conversion factors:

$$100 \cancel{\text{ gal}} \left(\frac{3.785 \cancel{\text{ L}}}{1 \cancel{\text{ gal}}}\right)\left(\frac{1000 \cancel{\text{ mL}}}{\cancel{\text{L}}}\right)\left(\frac{0.75 \cancel{\text{ g}}}{\cancel{\text{mL}}}\right)\left(\frac{1 \text{ mol}}{170.34 \cancel{\text{ g}}}\right) = 1.7 \times 10^3 \text{ mol } C_{12}H_{26}$$

C The total energy released is

$$\Delta H^\circ_{\text{comb}} = (-8086.5 \text{ kJ}/\cancel{\text{ mol}})(1.7 \times 10^3 \cancel{\text{ mol}}) = -1.4 \times 10^7 \text{ kJ}$$

From the balanced chemical equation for the reaction, we see that each mole of dodecane forms 12 mol of CO_2 upon combustion. Hence the amount of CO_2 emitted is

$$1.7 \times 10^3 \cancel{\text{ mol } C_{12}H_{26}} \left(\frac{\frac{24}{2} \cancel{\text{ mol } CO_2}}{1 \cancel{\text{ mol } C_{12}H_{26}}}\right)\left(\frac{44.0 \cancel{\text{ g}}}{1 \cancel{\text{ mol } CO_2}}\right)\left(\frac{1 \cancel{\text{ lb}}}{454 \cancel{\text{ g}}}\right)\left(\frac{1 \text{ tn}}{2000 \cancel{\text{ lb}}}\right) = 0.99 \text{ tn}$$

Exercise 7.9.2

Suppose the student in Example 7.9.2 couldn't afford the plane fare, so she decided to drive home instead. Assume that the round-trip distance by road was 5572 miles, her fuel consumption averaged 31 mpg, and her fuel was pure isooctane (C_8H_{18}, density = 0.6919 g/mL). How much energy was expended and how many tons of CO_2 were produced during her trip?

Answer available at the end of this section.

Summary

Thermochemical concepts can be used to calculate the efficiency of various forms of fuel, which can then be applied to environmental issues. More than 80% of the energy used by modern society (about 3×10^{17} kJ/yr) is from the combustion of fossil fuels. Because of their availability, ease of transport, and facile conversion to convenient fuels, natural gas and petroleum are currently the preferred fuels. Supplies of **coal**, a complex solid material derived from plants that lived long ago, are much greater, but the difficulty in transporting and burning a solid makes it less attractive as a fuel. Coal releases the smallest amount of energy per gram of any fossil fuel, and natural gas the greatest amount. The combustion of fossil fuels releases large amounts of CO_2 that upset the balance of the **carbon cycle** and result in a steady increase in atmospheric CO_2 levels. Because CO_2 is a **greenhouse gas**, which absorbs heat before it can be radiated from Earth into space, CO_2 in the atmosphere can result in increased surface temperatures (the **greenhouse effect**). The temperature increases caused by increased CO_2 levels because of human activities are, however, superimposed on much larger variations in Earth's temperature that have produced phenomena such as the ice ages and are still poorly understood.

Answers

Exercise 7.9.1

36 kg

Exercise 7.9.2

2.2×10^7 kJ; 1.6 tons of CO_2 (about twice as much as is released by flying)

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8: ELECTRONS IN ATOMS

Petrucci: *General Chemistry*
Principles and Modern Applications

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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.

8.1: Electromagnetic Radiation
8.2: Atomic Spectra
8.3: Quantum Theory
8.4: The Bohr Atom
8.5: Two Ideas Leading to a New Quantum Mechanics
8.6: Wave Mechanics
8.7: Quantum Numbers and Electron Orbitals
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8.1: Electromagnetic Radiation

Learning Objectives

- to learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves 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 8.1.1: 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 8.1.1). 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.

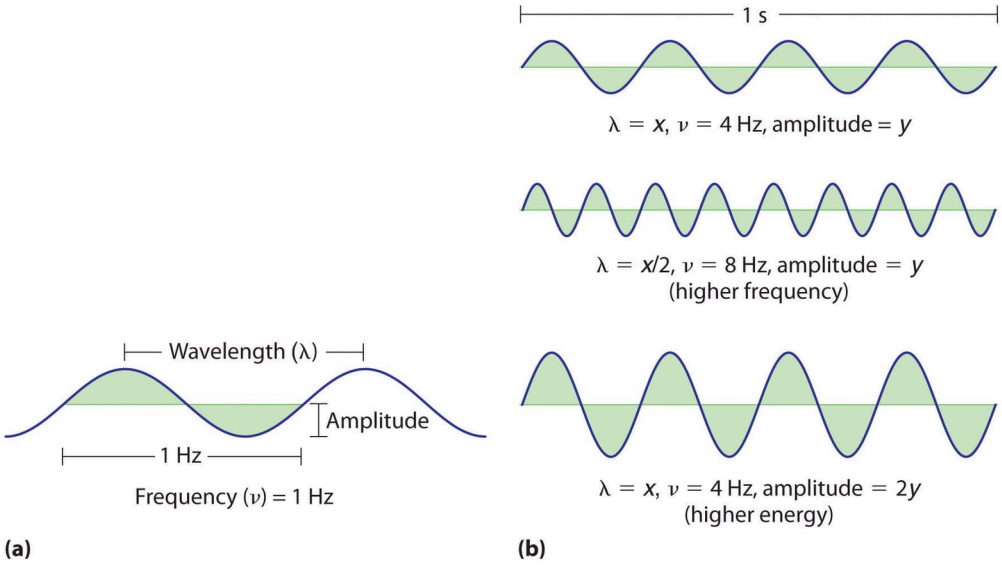


Figure 8.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 8.1.2). As you may have noticed in Figure 8.1.1, 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), distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs. λ is the lowercase Greek lambda, and u is the lowercase Greek nu. Wavelengths are described by a unit of distance, typically meters. The frequency (ν), the number of oscillations (i.e., of a wave) that pass a particular point in a given period of time. of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations persecond (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 (the vertical height of a wave, which is defined as half the peak-to-trough height), 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 8.1.2, 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), the distance traveled by a wave per unit time, 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:

$$(\text{wavelength})(\text{frequency}) = speed \tag{8.1.1}$$

$$\lambda u = v \tag{8.1.2}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{wave}}{second}\right) = \frac{meters}{second} \tag{8.1.3}$$

Be careful not to confuse the symbols for the speed, v, with the frequency, u. 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, which is energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure 8.1.3). Some forms of electromagnetic radiation are shown in Figure 8.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which is the speed with which all forms of electromagnetic radiation travel in a vacuum, a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (which is 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.

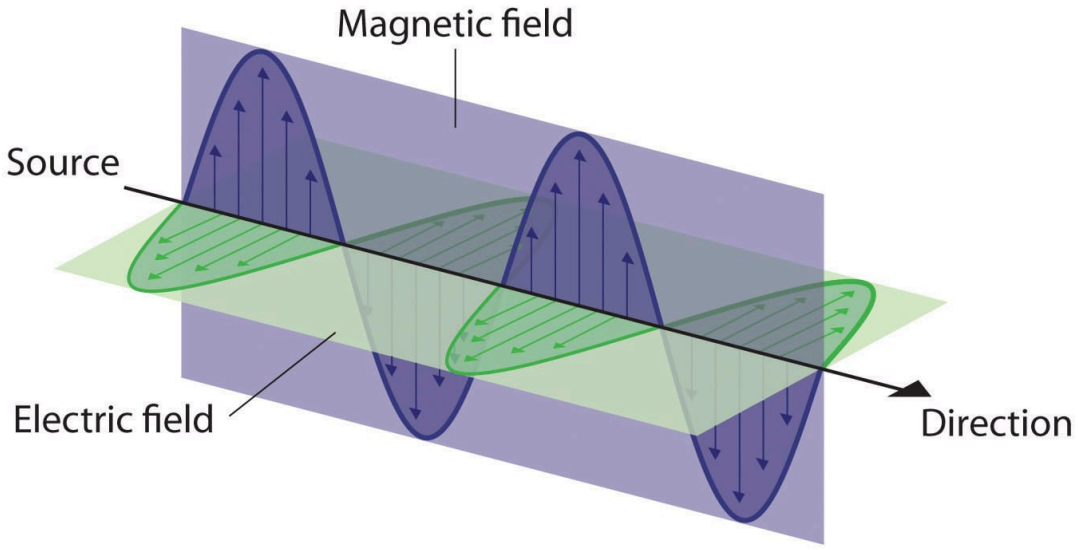


Figure 8.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (*c*), they differ in only wavelength and frequency. As shown in Figure 8.1.4 and Table 8.1.1, 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 8.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda u$$
$$u = \frac{c}{\lambda} \tag{8.1.4}$$

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.

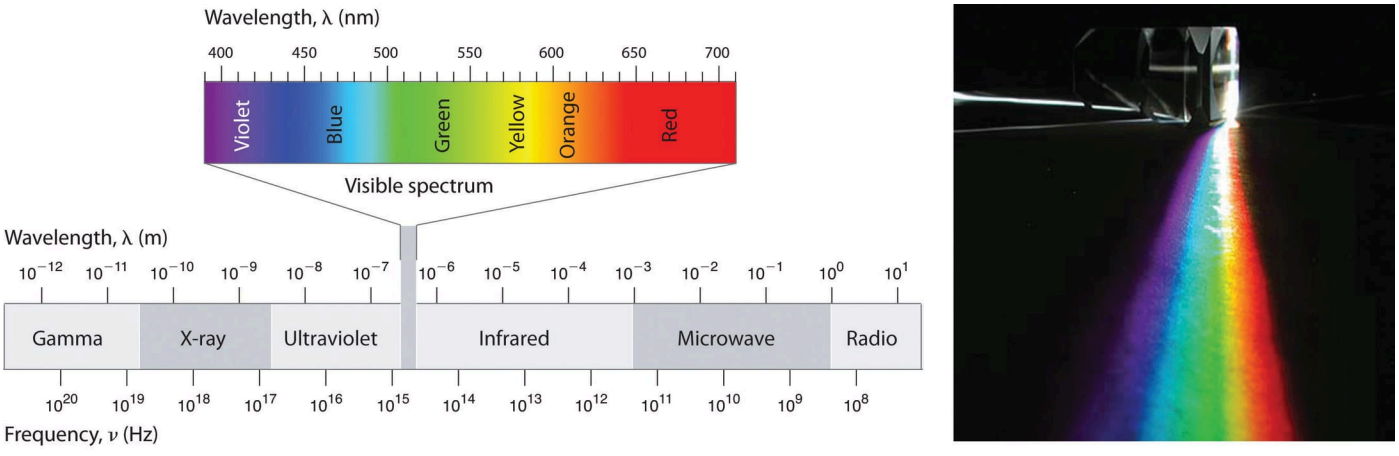


Figure 8.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum. (CC BY-NC-SA; anonymous)

Within this 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 8.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 8.1.1: 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}	x-ray
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:

$$E \propto u \tag{8.1.5}$$

$$E \propto \frac{1}{\lambda} \tag{8.1.6}$$

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 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.

Example 8.1.1

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 8.1.2 to calculate the wavelength in meters.

Solution:

From Equation 8.1.4, 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:

$$\lambda\nu = c = 2.998 \times 10^8 m/s \tag{8.1.7}$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{u} = \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \cancel{MHz}}\right)\left(\frac{1\ \cancel{MHz}}{10^6\ \cancel{s^{-1}}}\right) = 2.965\ m \tag{8.1.8}$$

Exercise 8.1.1

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: 8.45 mm

YouTube Video

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Electromagnetic Radiation: https://youtu.be/TZy7a69pP-w

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: **wavelength (λ)**, the distance between successive waves; **frequency (ν)**, 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.

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8.2: Atomic Spectra

Learning Objectives

- To know the relationship between atomic spectra and the electronic structure of atoms.

The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. The concept of the photon, however, emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. More direct evidence was needed to verify the quantized nature of electromagnetic radiation. In this section, we describe how experimentation 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, called a line spectrum, which is a spectrum in which light of only a certain wavelength is emitted or absorbed, rather than a continuous range of wavelengths (Figure 8.2.1), rather than a continuous range of colors. 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.

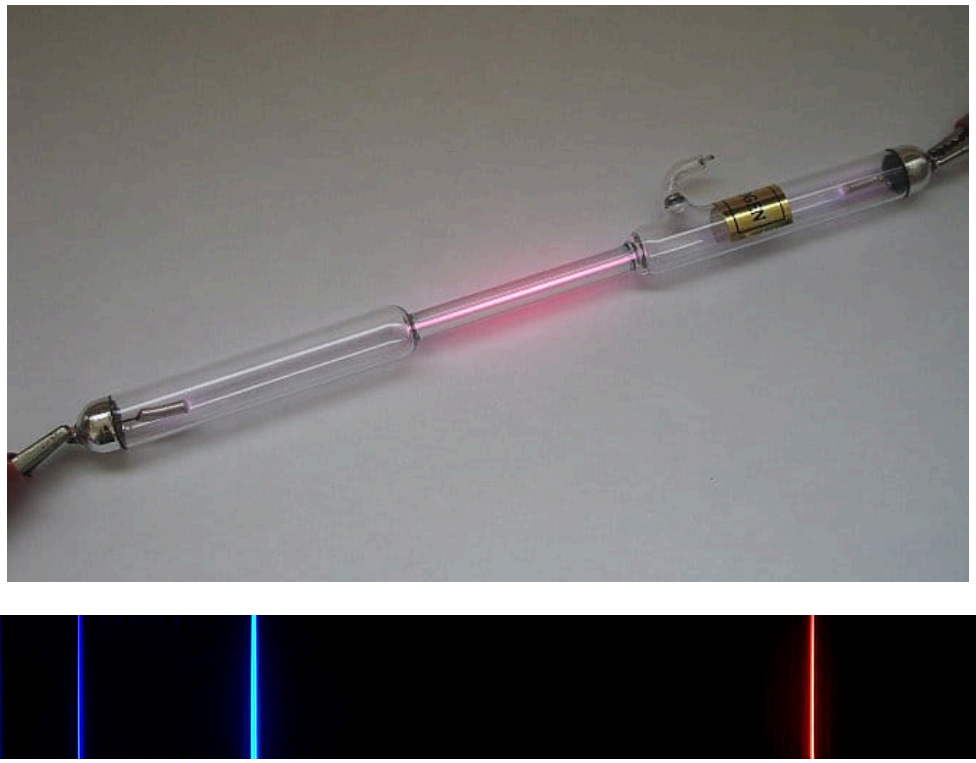




Figure 8.2.1: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm.

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 the observation of only a few values of λ (or ν) 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:

$$u = constant\ \left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{8.2.1}$$

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*:

$$\frac{1}{\lambda} = \Re\ \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{8.2.2}$$

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 described 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.

YouTube Video

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The Bohr Atom: https://youtu.be/GuFQEOzFOgA

Summary

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 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.

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. Bohr's model could not, however, explain the spectra of atoms heavier than hydrogen.

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8.3: Quantum Theory

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 whose wavelength and color that depends on the temperature of the object. The wavelength of energy emitted by an object 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 8.3.1: 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 8.3.2. 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 8.3.2. 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 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 8.3.2, 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 (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum..

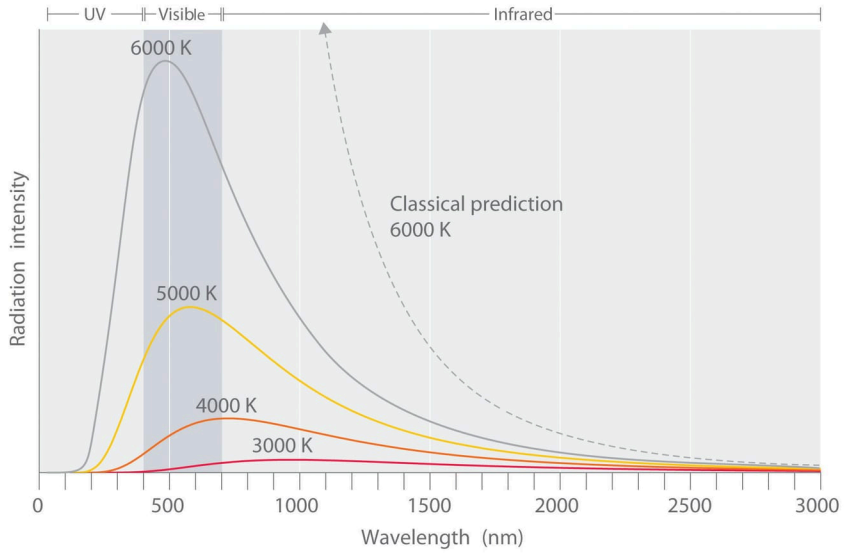
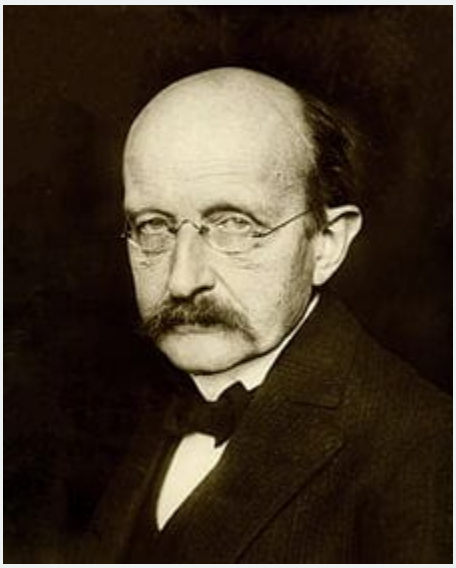


Figure 8.3.2: Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure 8.3.1 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 8.3.1). 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 Max Planck (1858–1947) by the equation

$$E = hu \tag{8.3.1}$$

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:

$$h = 6.626 \times 10^{-34} \text{ J•s (joule-seconds)}$$

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 8.3.2. 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 8.3.2, 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.

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 8.3.3). 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).

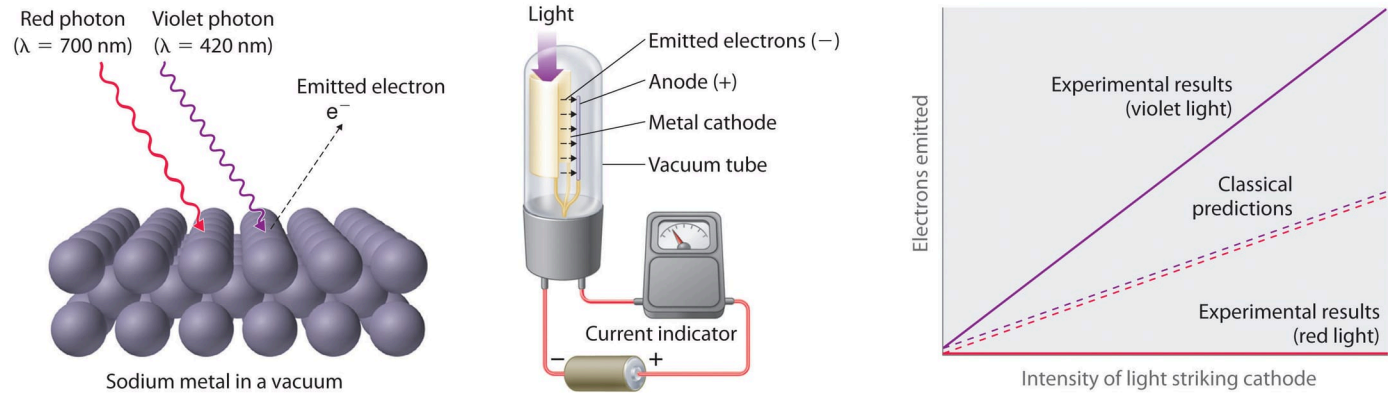


Figure 8.3.3: The Photoelectric Effect *(a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons 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 8.3.1 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 ($E_o = h\nu_o$). 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:

$$kinetic\ energy\ of\ ejected\ electron = E - E_o = hu - hu_o = h\,(u - u_o) \tag{8.3.2}$$

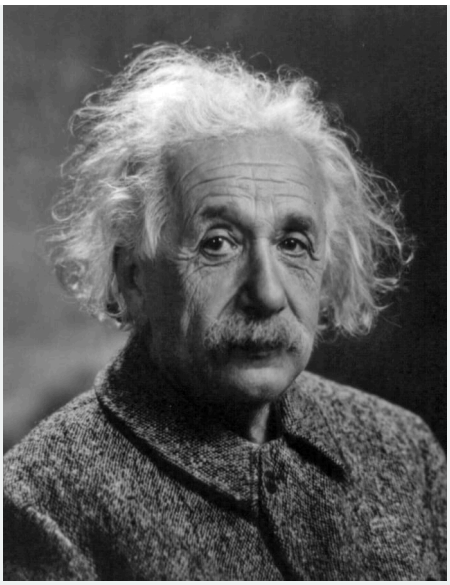
When a metal is struck by light with energy above the threshold energy E_o, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the number of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *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.



Figure 8.3.4: 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 8.3.1

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 8.3.4). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

A. Use Equation 6.1.2 and Equation 8.3.1 to calculate the energy in joules.

Solution:

The energy of a single photon is given by $E = h\nu = hc/\lambda$.

Exercise 8.3.1

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. $1.287 \times 10^{-15}\ J/photon$
b. 4497 times

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 Photoelectric Effect: https://youtu.be/mxBMxJLauQk

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, $E = h\nu$. Both energy and matter have fundamental building blocks: quanta and atoms, respectively.

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8.4: The Bohr Atom

Learning Objectives

- To know the relationship between atomic spectra and the electronic structure of atoms.

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

$$E_n = \frac{-\Re hc}{n^2} \tag{8.4.1}$$

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.

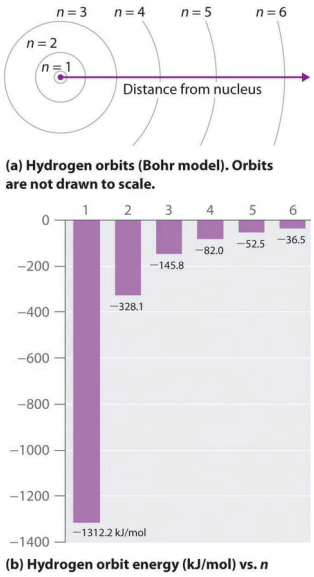
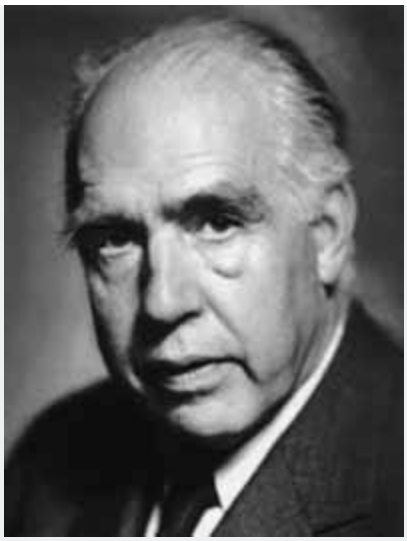


Figure 8.4.2 The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing *n*. (b) The energy of the orbit becomes increasingly less negative with increasing *n*.

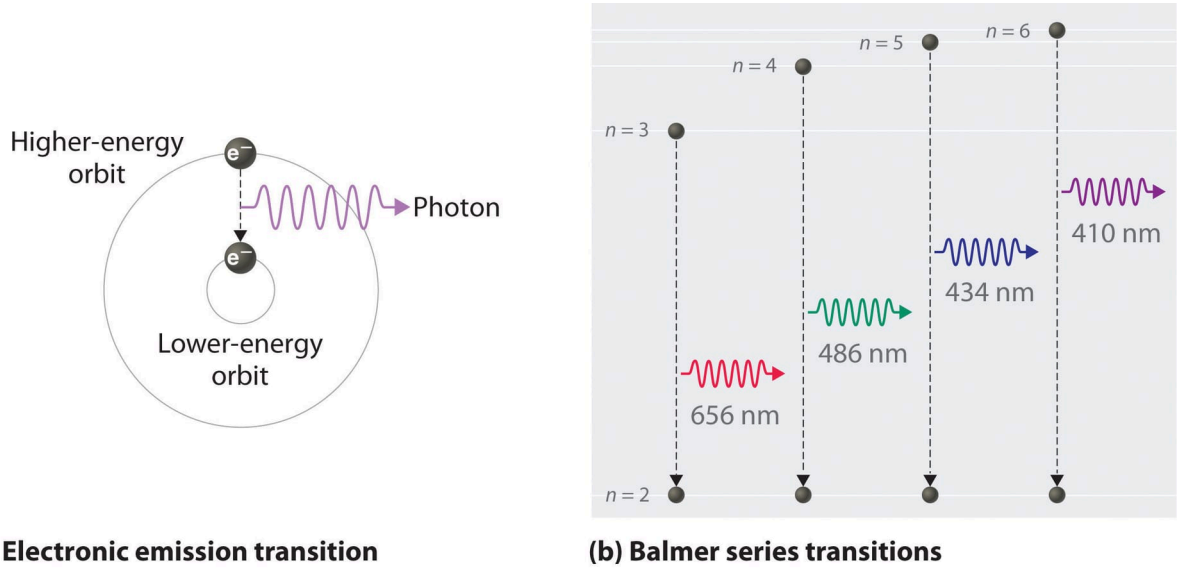
Niels Bohr (1885–1962)

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 $8.4.3$ indicates that the electron-nucleus pair is more tightly bound 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), the most stable arrangement 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 2.10). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an excited state. Any arrangement of electrons that is higher in energy than the ground state.: its energy is higher than the energy of 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 $8.4.1$).



(a) Electronic emission transition **(b) Balmer series transitions**

Figure $8.4.3$: 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 (Δ*E*) 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 8.4.3) for each energy value gives

$$\Delta E = E_{final} - E_{initial} = -\frac{\Re hc}{n_2^2} - \left(-\frac{\Re hc}{n_1^2}\right) = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{8.4.2}$$

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 8.4.3. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{8.4.3}$$

Canceling hc on both sides gives

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{8.4.4}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equation 8.4.5 and Equation 8.4.6 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 (part (b) in Figure 2.9). As shown in part (b) in Figure 8.4.3, 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 (part (a) in Figure 8.4.3). 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 (part (a) in Figure 8.4.1). 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 8.4.4

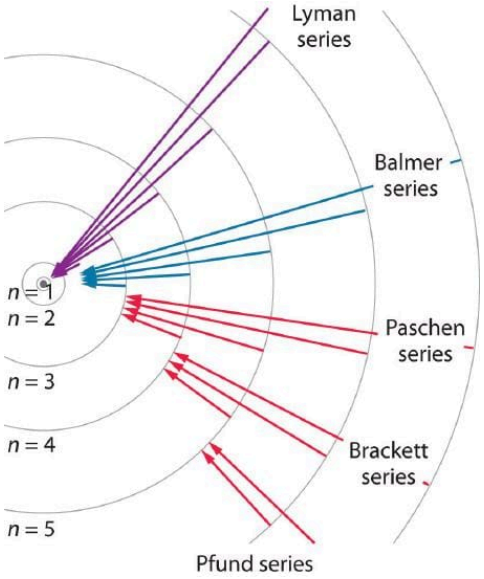


Figure 8.4.4: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to 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.)

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 8.4.1: 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 8.4.2 (the Rydberg equation) and solve for λ.
B. Use Figure 8.4.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{8.4.5}$$

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.

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1} \tag{8.4.6}$$

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}.

$$\varpi = \frac{1}{\lambda} = 8.228 \times 10^6\ \cancel{m}^{-1}\left(\frac{\cancel{m}}{100\ cm}\right) = 82,280\ cm^{-1} \tag{8.4.7}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm \tag{8.4.8}$$

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 8.4.1: 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: 4.65 × 10^3 nm; infrared

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:

- 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.

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 8.4.5). 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.

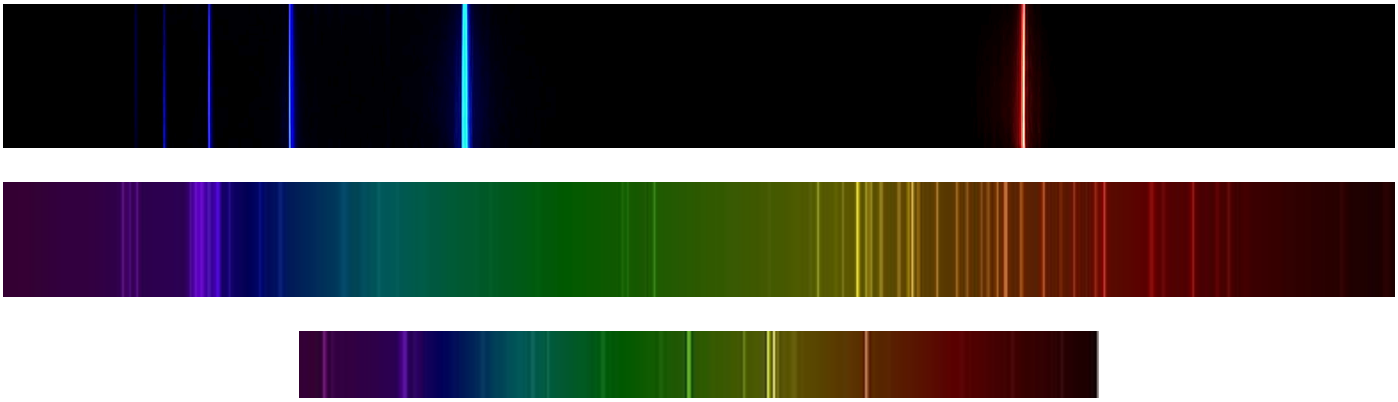


Figure 8.4.5: The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown.

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). Because each element has characteristic emission and absorption spectra, scientists can use such spectra to analyze the composition of matter.

> 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.

The Energy States of the Hydrogen Atom

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.

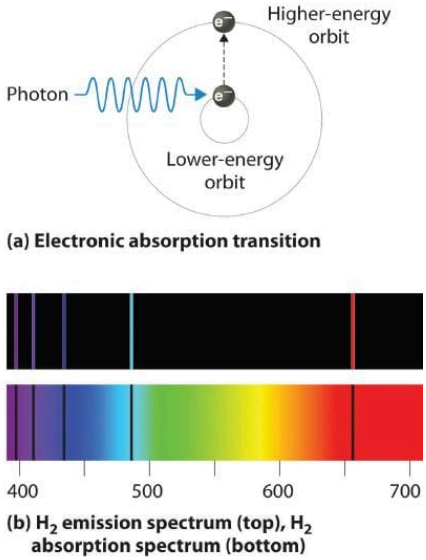


Figure 8.4.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.

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 8.4.7 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.

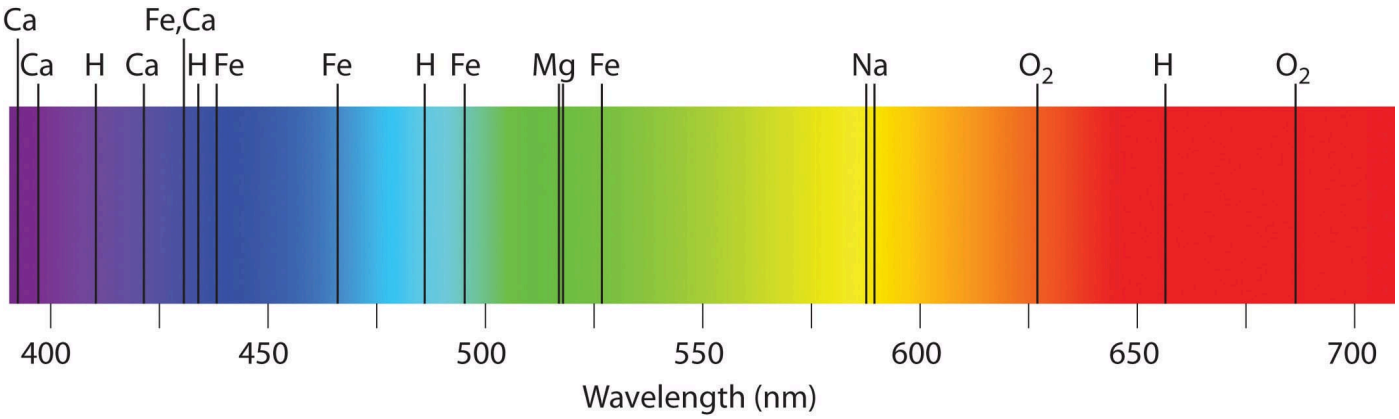


Figure 8.4.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere.

The familiar red color of "neon" signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 8.4.5. 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 8.4.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

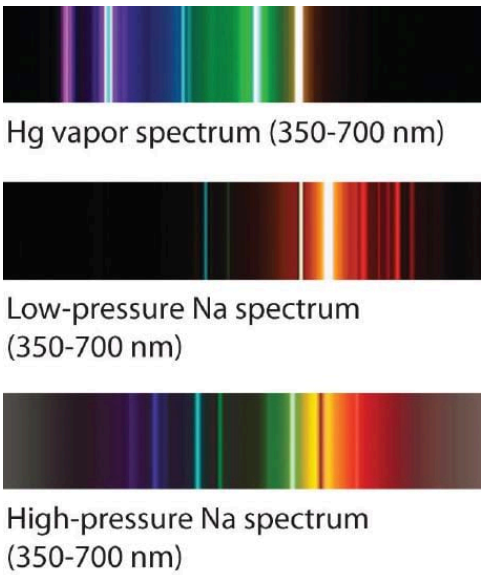


Figure 8.4.8: The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. 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.

YouTube Video

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The Bohr Atom: https://youtu.be/GuFQEOzFOgA

The Chemistry of Fireworks

The colors of fireworks are also due to atomic emission spectra. As shown in part (a) in Figure 8.4.9, a typical shell used in a fireworks display contains gunpowder to propel the shell into the air and a fuse to initiate a variety of reactions that produce heat and small explosions. Thermal energy excites the atoms to higher energy states; as they decay to lower energy states, the atoms emit light that gives the familiar colors.



Figure 8.4.9 :The Chemistry of Fireworks *(a) In the "multibreak" shell used for fireworks, the chambers contain mixtures of fuels and oxidizers plus compounds for special effects ("stars") connected by time-delay fuses so that the chambers explode in stages. (b) The finale of a fireworks display usually consists of many shells fired simultaneously to give a dazzling multicolor display. The labels indicate the substances that are responsible for the colors of some of the fireworks shown.*

When oxidant/reductant mixtures listed in Table 8.4.1 are ignited, a flash of white or yellow light is produced along with a loud bang. Achieving the colors shown in part (b) in Figure 8.4.9 requires adding a small amount of a substance that has an emission spectrum in the desired portion of the visible spectrum. For example, sodium is used for yellow because of its 589 nm emission lines. The intense yellow color of sodium would mask most other colors, so potassium and ammonium salts, rather than sodium salts, are usually used as oxidants to produce other colors, which explains the preponderance of such salts in Table 8.4.1 . Strontium salts, which are also used in highway flares, emit red light, whereas barium gives a green color. Blue is one of the most difficult colors to achieve. Copper(II) salts emit a pale blue light, but copper is dangerous to use because it forms highly unstable explosive compounds with anions such as chlorate. As you might guess, preparing fireworks with the desired properties is a complex, challenging, and potentially hazardous process. If you have the time here is a NOVA program about how fireworks are made.

*Table 8.4.1: Common Chemicals Used in the Manufacture of Fireworks**

Oxidizers	Fuels (reductants)	Special effects
ammonium perchlorate	aluminum	*blue flame*: copper carbonate, copper sulfate, or copper oxide
barium chlorate	antimony sulfide	*red flame*: strontium nitrate or strontium carbonate
barium nitrate	charcoal	*white flame*: magnesium or aluminum
potassium chlorate	magnesium	*yellow flame*: sodium oxalate or cryolite (Na_3AlF_6)
potassium nitrate	sulfur	*green flame*: barium nitrate or barium chlorate
potassium perchlorate	titanium	*white smoke*: potassium nitrate plus sulfur
strontium nitrate		*colored smoke*: potassium chlorate and sulfur, plus organic dye
		whistling noise: potassium benzoate or sodium salicylate
		white sparks: aluminum, magnesium, or titanium
		gold sparks: iron fillings or charcoal

***Almost any combination of an oxidizer and a fuel may be used along with the compounds needed to produce a desired special effect.**

YouTube Video

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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. Bohr's model could not, however, explain the spectra of atoms heavier than hydrogen.

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8.5: Two Ideas Leading to a New Quantum Mechanics

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 following equation:

$$E = h\nu = h\frac{c}{\lambda} = mc^2 \tag{8.5.1}$$

According to this theory, a photon of wavelength λ and frequency ν has a nonzero mass, which is given as follows:

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2} = \frac{h}{\lambda c} \tag{8.5.2}$$

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

$$\lambda = \frac{h}{mv} \tag{8.5.3}$$

where

- 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 8.5.1, 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.

Example 8.5.1

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 8.5.3 and solve for the wavelength.

Solution:

The wavelength of a particle is given by λ = *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

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} = \frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}^{\cancel{-2}} \cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m} \cdot \cancel{s^{-1}}\right)} = 9.95 \times 10^{-35}\ m \tag{8.5.4}$$

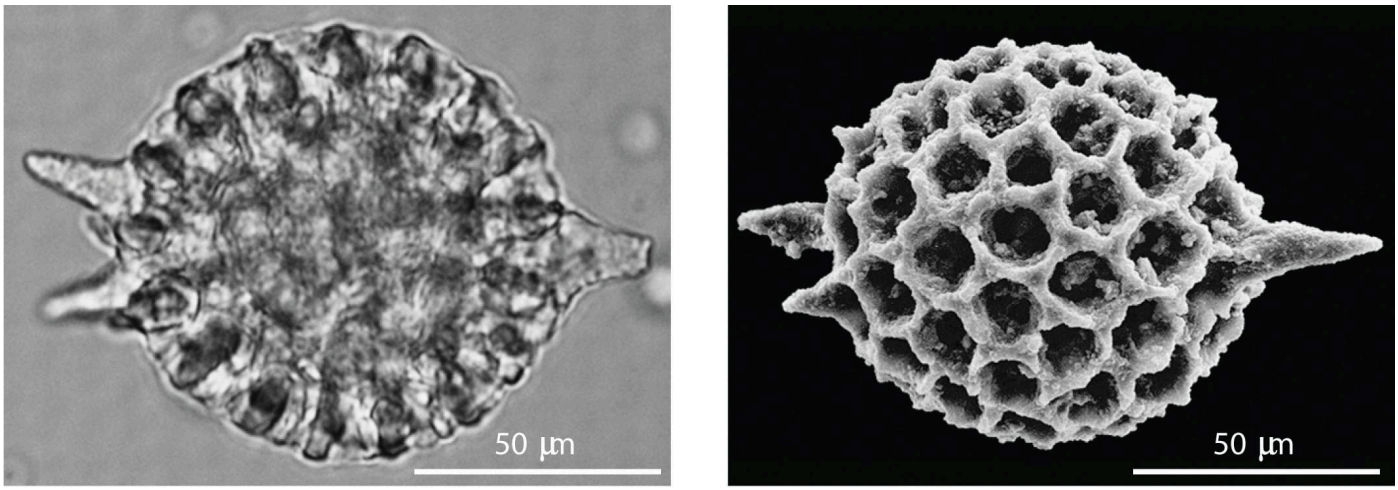
(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

Exercise 8.5.1

Calculate the wavelength of a neutron that is moving at 3.00 × 10^3 m/s.

Answer: 1.32 Å, or 132 pm

As you calculated in Example 8.5.1, 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, 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 8.5.1).



(a) Radiolarian under light microscope **(b) Radiolarian under electron microscope**

Figure 8.5.1: 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

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 8.5.2a, on the right shows an arbitrary phase difference between two wave. Figure 8.5.2b shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 8.5.2c 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.

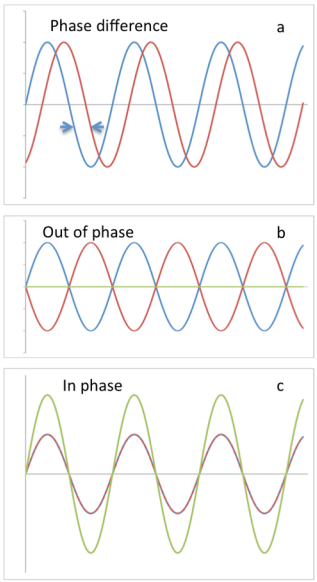


Figure 8.5.2: Phase. Two waves traveling together are displaced by a phase difference. If the phase difference is 0 then they lay on top of each other and reinforce. If the phase difference is 180 they completely cancel each other out.

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 8.5.3). If the length of the string is *L*, then the lowest-energy vibration (the fundamental (the lowest-energy standing wave) has wavelength

$$\frac{\lambda}{2} = L$$
$$\lambda = 2L \tag{8.5.5}$$

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

$$\lambda = \frac{2L}{n} \tag{8.5.6}$$

where *n* has any integral value. Thus the resonant vibrational energies of the string are quantized. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. By analogy we can think of the resonant frequencies as being quantized. Notice in Figure 8.5.3 that all overtones have one or more nodes (the points where the amplitude of a wave is zero), points where the string does not move. The amplitude of the wave at a node is zero.

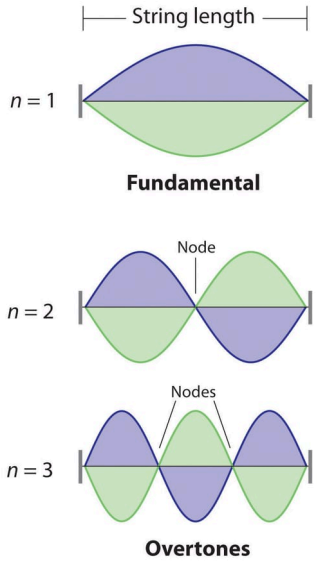


Figure 8.5.3 Standing Waves on a Vibrating String. The vibration with *n* = 1 is the fundamental and contains no nodes. Vibrations with higher values of *n* are called overtones; they contain *n* – 1 nodes.

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

$$2\pi r = n\lambda \tag{8.5.7}$$

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 8.5.4). 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 non resonant 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 8.5.2, one complete wavelength would close the circle. Higher energy levels would have successively higher values of *n* with a corresponding number of nodes.

Standing waves are often observed on rivers, reservoirs, ponds, and lakes when seismic waves from an earthquake travel through the area. The waves are called *seismic seiches*, a term first used in 1955 when lake levels in England and Norway oscillated from side to side as a result of the Assam earthquake of 1950 in Tibet. They were first described in the Proceedings of the Royal Society in 1755 when they were seen in English harbors and ponds after a large earthquake in Lisbon, Portugal. Seismic seiches were also observed in many places in North America after the Alaska earthquake of March 28, 1964. Those occurring in western

reservoirs lasted for two hours or longer, and amplitudes reached as high as nearly 6 ft along the Gulf Coast. The height of seiches is approximately proportional to the thickness of surface sediments; a deeper channel will produce a higher seiche.

Still, as 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.

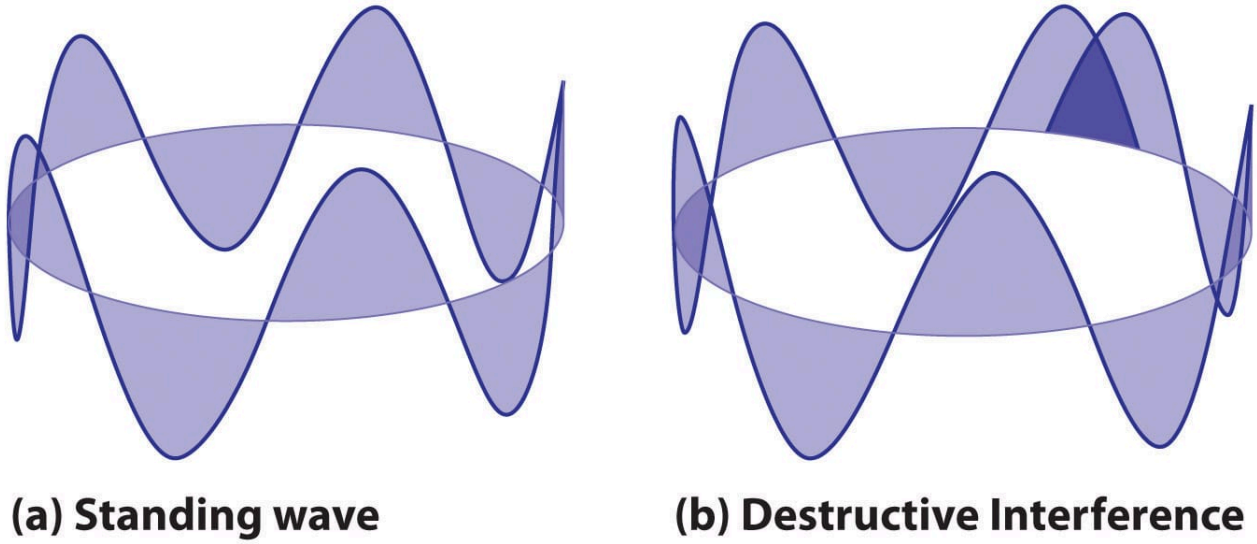


Figure 8.5.4 Standing Circular Wave and Destructive Interference.(a) In a standing circular wave with n = 5, the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of 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.

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 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.

YouTube Video

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The de Broglie Equation: https://youtu.be/pz0zMHWtK7Q

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 as shown in the video below. 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.

Heisenberg's uncertainty principle for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. DeBroglie's idea of wave particle duality means that particles such as electrons which all exhibit wave like characteristics, will also undergo diffraction from slits whose size is of the order of the electron wavelength.

YouTube Video

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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 is greater than or equal to Planck's constant *h* divided by 4π: states that the uncertainty in the position of a particle (Δ*x*) multiplied by the uncertainty in its momentum [Δ(*mv*)] is greater than or equal to Planck's constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{8.5.8}$$

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 (Δ*x* = 0), then the uncertainty in its momentum must be infinite:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{8.5.9}$$

Because the mass of the electron at rest (*m*) is both constant and accurately known, the uncertainty in Δ(*mv*) must be due to the Δ*v* term, which would have to be infinitely large for Δ(*mv*) to equal infinity. That is, according to Equation 8.5.8, the more accurately we know the exact position of the electron (as $\Delta x \rightarrow 0$), the less accurately we know the speed and the kinetic energy of the electron (1/2 mv^2) because $\Delta(mv) \rightarrow \infty$. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as $\Delta(mv) \rightarrow 0$], then $\Delta x \rightarrow \infty$ 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 8.5.2

Calculate the minimum uncertainty in the position of the pitched baseball from Example 8.5.1 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 8.5.7) 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 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 $h = 6.626 \times 10^{-34}$ J•s and $m = 0.149$ kg. Because there is no uncertainty in the mass of the baseball, $\Delta(mv) = m\Delta v$ and $\Delta v = \pm 1$ mi/h. We have

$$\Delta v = \left(\frac{1\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 0.4469\ \ m/s$$

C Therefore,

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ J \cdot s}{4\,(3.1416)}\right)\left(\frac{1}{(0.149\ kg)\,(0.4469\ m \cdot s^{-1})}\right)$$

Inserting the definition of a joule (1 J = 1 kg•m^2/s^2) gives

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot s}{4\,(3.1416)\left(\cancel{s^2}\right)}\right)\left(\frac{1\ \cancel{s}}{\left(0.149\ \cancel{kg}\right)(0.4469\ \cancel{m})}\right)$$

$$\Delta x \geqslant 7.92 \pm \times 10^{-34}\ \ m$$

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 8.5.2

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: 6 × 10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

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.

$$\lambda = \frac{h}{mv} \tag{8.5.3}$$

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.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{8.5.7}$$

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8.6: Wave Mechanics

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. In doing so, Schrödinger developed the theory of quantum mechanics, which is used today to describe the energies and spatial distributions of electrons in atoms and molecules.

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 *wave functions* that are the solutions of Schrödinger's equations.

Wave Functions

A wave function (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 wave function is associated with a particular energy E. The properties of wave functions derived from quantum mechanics are summarized here:

- **A wave function 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 wanted 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 8.6.1). 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.

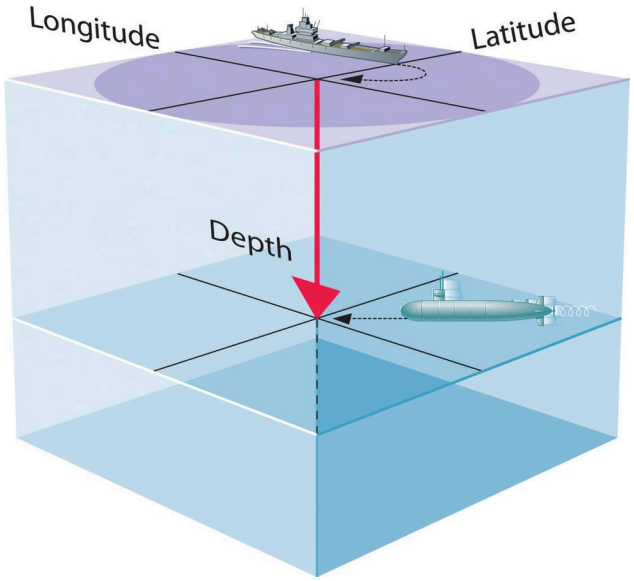


Figure 8.6.1: The Four Variables (Latitude, Longitude, Depth, and Time) Required to Precisely Locate an Object

If you are the captain of a ship trying to intercept an enemy submarine, you need to deliver your depth charge to the right location at the right time.

- **The magnitude of the wave function at a particular point in space is proportional to the amplitude of the wave at that point.** Many wave functions 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 wave function (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 wave function should *not* be confused with a positive or negative electrical charge.
- **The square of the wave function 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 wave function (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wave function 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 8.6.2.

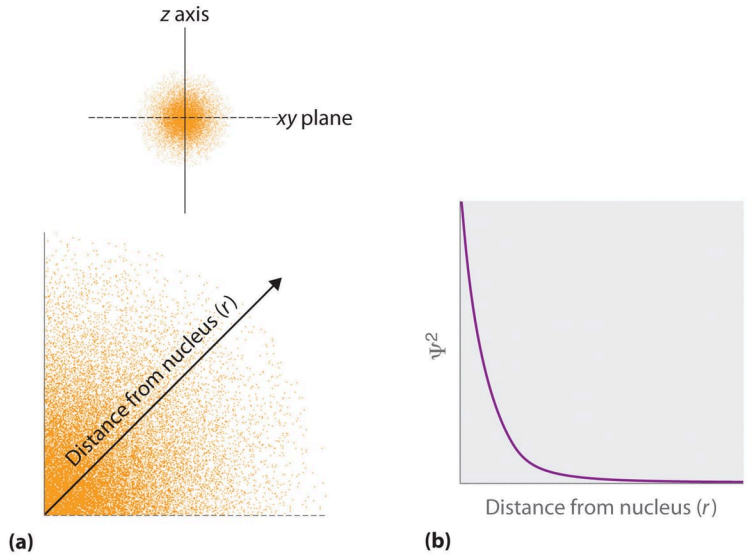


Figure 8.6.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at $r = 0$ (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.

- **Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wave function.** From the patterns of one- and two-dimensional standing waves shown in Figure 6.18 and Figure 6.19, 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 wave functions. 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 (wave functions), each of which is specified by a set of numbers called quantum numbers.
- **Each wave function 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.

Quantum Numbers

Schrödinger's approach uses three quantum numbers (n, l, and m_l) to specify any wave function. 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.

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Introduction to Quantum Numbers: https://youtu.be/07JpBeaPxL8

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \ldots \tag{8.6.1}$$

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 wave functions 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:

$$l = 0, 1, 2, \ldots, n - 1 \tag{8.6.2}$$

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 wave functions 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.

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Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell: https://youtu.be/ms7WR149fAY

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:

$$m_l = -l, -l + 1, \ldots, 0, \ldots, l - 1, l \tag{8.6.3}$$

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 wave function 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.

Example 8.6.1: 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:

Exercise 8.6.1: n=3 Shell Structure

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer: three subshells; nine orbitals

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:

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 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 8.6.1):

- 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.

Note

Each principal shell has n subshells, and each subshell has $2l + 1$ orbitals.

Table 8.6.1 *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	2s	0	1	4
	1	2p	–1, 0, 1	3	
3	0	3s	0	1	9
	1	3p	–1, 0, 1	3	
	2	3d	–2, –1, 0, 1, 2	5	
4	0	4s	0	1	16
	1	4p	–1, 0, 1	3	
	2	4d	–2, –1, 0, 1, 2	5	
	3	4f	–3, –2, –1, 0, 1, 2, 3	7	

YouTube Video

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Magnetic Quantum Number (m_l) & Spin Quantum Number (m_s): https://youtu.be/gbmGVUXBOBk

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 **wave functions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wave functions have five important properties:

1. the wave function uses three variables (Cartesian axes *x*, *y*, and *z*) to describe the position of an electron;
2. the magnitude of the wave function 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 wave function 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 wave function; and
5. each spatial distribution of the electron described by a wave function 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 wave functions 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. Wave functions 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 wave function 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**.

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8.7: Quantum Numbers and Electron Orbitals

08: The quantum hydrogen atom

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8.8: Interpreting and Representing the Orbitals of the Hydrogen Atom

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8.9: Electron Spin: A Fourth Quantum Number

Learning Objectives

- To introduce the concept of electron spin and demonstrated it is quantized

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. 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.

The Stern-Gerlach Experiment

The quantum numbers $n,\ l,\ m$ are not sufficient to fully characterize the physical state of the electrons in an atom. In 1926, Otto Stern and Walther Gerlach carried out an experiment that could not be explained in terms of the three quantum numbers $n,\ l,\ m$ and showed that there is, in fact, another quantum-mechanical degree of freedom that needs to be included in the theory. The experiment is illustrated in the figure 8.9.1. A beam of atoms (e.g. hydrogen or silver atoms) is sent through a spatially inhomogeneous magnetic field with a definite field gradient toward one of the poles. It is observed that the beam splits into two beams as it passes through the field region.

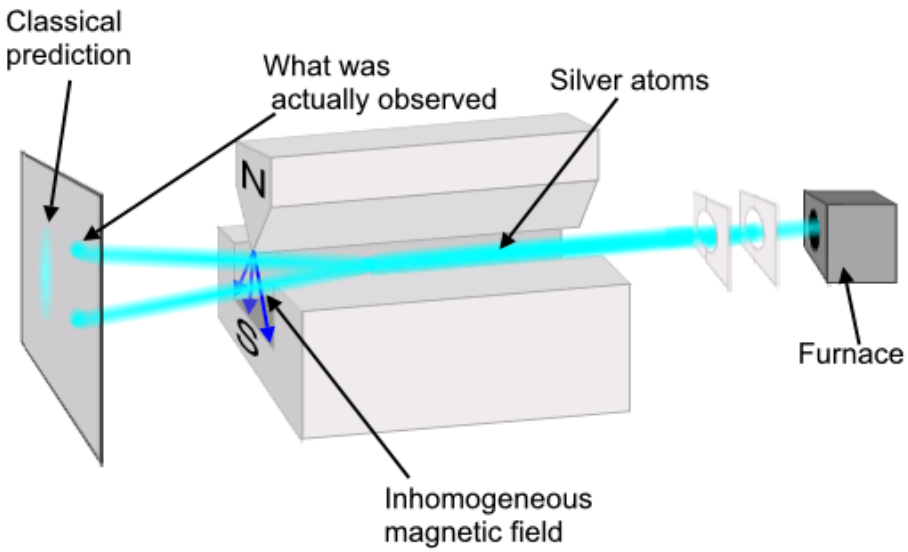


Figure $8.9.1$: The Stern-Gerlach apparatus. from Wikipedia

The fact that the beam splits into 2 beams suggests that the electrons in the atoms have a degree of freedom capable of coupling to the magnetic field. That is, an electron has an *intrinsic magnetic moment* M arising from a degree of freedom that has no classical analog. The magnetic moment must take on only 2 values according to the Stern-Gerlach experiment. The intrinsic property that gives rise to the magnetic moment must have some analog to a *spin*, S; unlike position and momentum, which have clear classical analogs, spin does not.

The implication of the Stern-Gerlach experiment is that we need to include a fourth quantum number, m_s in our description of the physical state of the electron. That is, in addition to give its principle, angular, and magnetic quantum numbers, we also need to say if it is a spin-up electron or a spin-down electron.

Electron Spin

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.

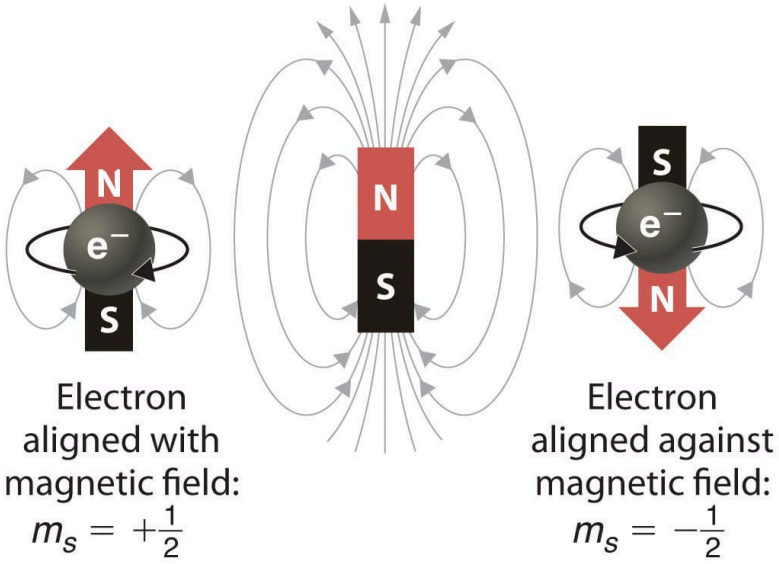


Figure 8.9.2: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure 8.9.2). 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 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 8.9.2

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 2*p* orbital and predict the maximum number of electrons the 2*p* 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 8.9.2

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: (6, 0, 0, +½), (6, 0, 0, –½); two electrons

Summary

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).

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8.10: Multielectron Atoms

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 6.29, 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:

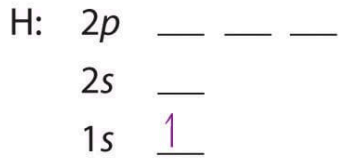
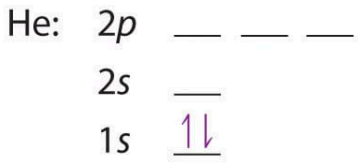


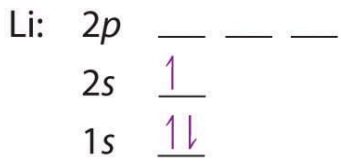
Figure 6.29"), and the electron configuration is written as $1s^1$ and read as "one-s-one."

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



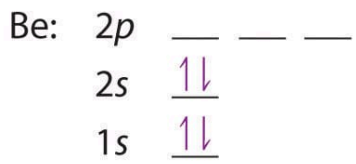
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

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. Figure 6.29 tells us that the next lowest energy orbital is 2s, so the orbital diagram for lithium is

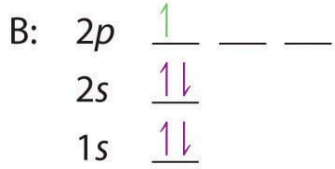


This electron configuration is written as $1s^2 2s^1$.

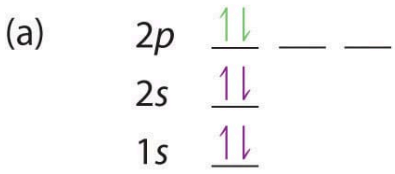
The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1s and 2s orbitals to achieve a $1s^2 2s^2$ electron configuration:

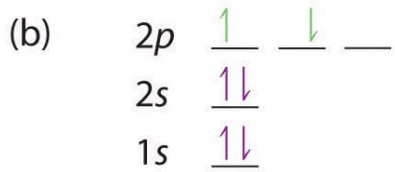


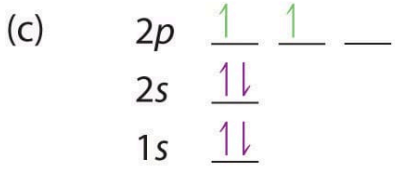
When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Because all three 2*p* orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2 2s^2 2p^1$:



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?

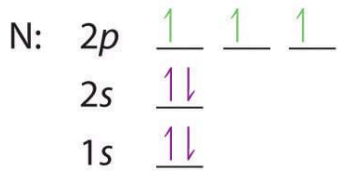






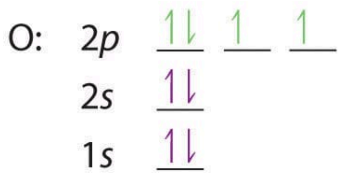
Because of electron-electron repulsions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because 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

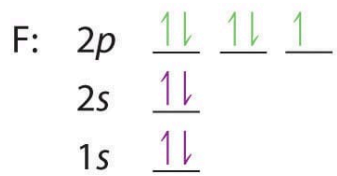


with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

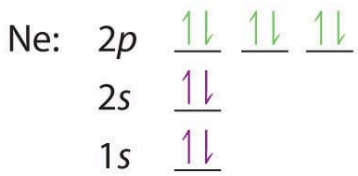
At oxygen, with Z = 8 and eight electrons, we have no choice. One electron must be paired with another in one of the 2*p* orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration. Because all the 2*p* orbitals are degenerate, it doesn't matter which one has the pair of electrons.



Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:



When we reach neon, with Z = 10, we have filled the 2*p* subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:



Notice that for neon, as for helium, all the orbitals through the 2*p* 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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Electron Configuration of Atoms: https://youtu.be/LlY-O3-bfnk

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 $[Ne]3s^1$:

Neon	Z = 10	$1s^2 2s^2 2p^6$
Sodium	Z = 11	$1s^2 2s^2 2p^6 \mathbf{3}s^1 = [Ne]\mathbf{3}s^1$

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:

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 8.10.2

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 6.29, 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 6.29 tells us are the 3*s* and 3*p* orbitals:

P: [Ne] 3*p* ___ ___ ___
3*s* ___

Because the 3s orbital is lower in energy than the 3*p* orbitals, we fill it first:

P: [Ne] 3*p* ___ ___ ___
3*s* ↑↓

Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:

P: [Ne] 3*p* 1 1 1
3*s* ↑↓

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 8.10.2

Draw an orbital diagram and use it to derive the electron configuration of chlorine, Z = 17. What is its valence electron configuration?

Answer: [Ne]$3s^2 3p^5$; $3s^2 3p^5$

YouTube Video

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Definition of Valence Electrons: https://youtu.be/_ldxOYwM2VM

The general order in which orbitals are filled is depicted in Figure 8.10.1. 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 3*d* 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 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* 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, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5s, 4*d*, and 5*p* orbitals are filled sequentially.

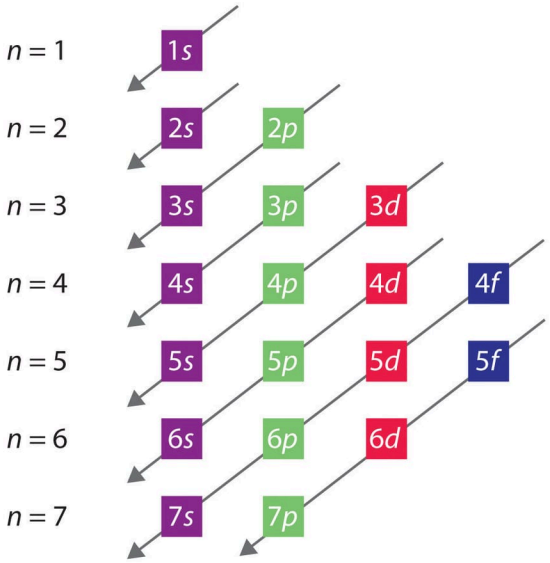


Figure 8.10.1 Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to 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 6*s* 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 (and last known) 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 7*s* 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 8.10.3

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 8.10.1 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 8.10.1 and using the periodic table as a guide, we obtain

$1s^2$	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
	row 1–5	54 electrons

After filling the first five rows, we still have 80 – 54 = 26 more electrons to accommodate. According to Figure 8.10.2, 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 8.10.3

Although element 114 is not stable enough to occur in nature, two isotopes of element 114 were created for the first time in a nuclear reactor in 1999 by a team of Russian and American scientists. Write the complete electron configuration for element 114.

Answer: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^2$

The electron configurations of the elements are presented in Figure 8.10.3, 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 8.10.1. 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. 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 some of the additional anomalies indicated in Figure 8.10.3. 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.

Note

Additional stability is associated with half-filled or filled subshells.

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**.

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8.11: Electron Configurations

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8.12: Electron Configurations and the Periodic Table

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9: THE PERIODIC TABLE AND SOME ATOMIC PROPERTIES

Petrucci: *General Chemistry*
Principles and Modern Applications

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9.1: Classifying the Elements: The Periodic Law and the Periodic Table

Learning Objectives

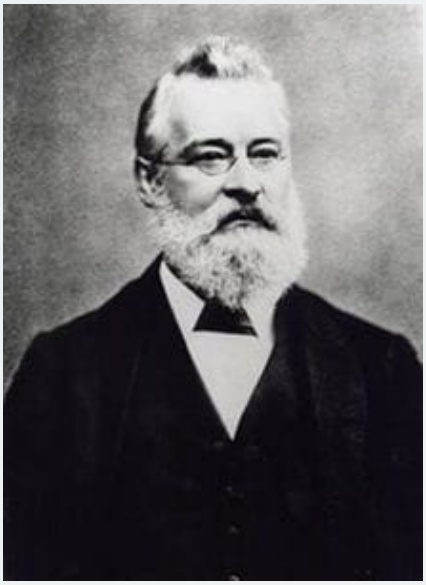
- To become familiar with the history of the periodic table.

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.

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 9.1.1). (The noble gases were still unknown.) Newlands therefore suggested that the elements could be classified into octaves A group of seven elements, corresponding to the horizontal rows in the main group elements (not counting the noble gases, which were unknown at the time)., corresponding to the *horizontal* rows in the main group elements. 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.

Note: 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.



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 9.1.1: 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."

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 9.1.2), 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):

$$\frac{molar\ mass\ \left(\not{g}/mol\right)}{density\ \left(\not{g}/cm^3\right)} = molar\ volume\ \left(cm^3/mol\right) \tag{9.1.1}$$

As shown in Figure 9.1.2, 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.

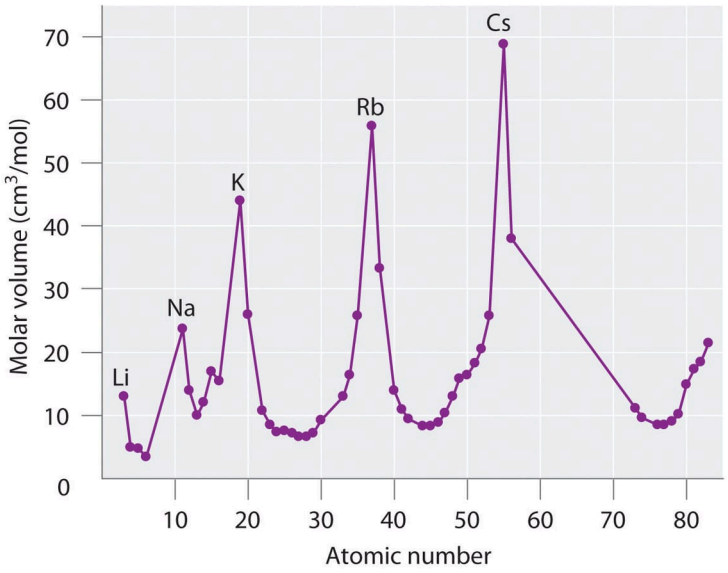
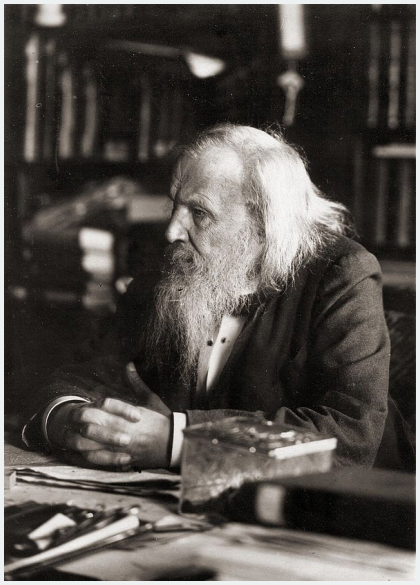


Figure 9.1.2: Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of 1870. *Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).*

Note: 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

Mendeleev, who first published his periodic table in 1869 (Figure 9.1.3), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements and that of Meyer and others is that Mendeleev did not assume that all the elements had been discovered (actually, only about two-thirds of the naturally occurring elements were known at the

time). Instead, he deliberately left blanks in his table at atomic masses 44, 68, 72, and 100, in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.

Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	— =68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce= 40	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Figure 9.1.3: Mendeleev's Periodic Table, as Published in the German Journal *Annalen der Chemie und Pharmacie* in 1872. The column headings "Reihen" and "Gruppe" are German for "row" and "group." Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.

The groups in Mendeleev's table are determined by how many oxygen or hydrogen atoms are needed to form compounds with each element. For example, in Group I, two atoms of hydrogen, lithium, Li, sodium, Na, and potassium form compounds with one atom of oxygen. In Group VII, one atom of fluorine, F, chlorine, Cl, and bromine, Br, react with one atom of hydrogen. Notice how this approach has trouble with the transition metals. Until roughly 1960, a rectangular table developed from Mendeleev's table and based on reactivity was standard at the front of chemistry lecture halls.

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table 9.1.1). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, *eka*-aluminum and *eka*-silicon (from the Sanskrit *eka*, meaning "one," as in "one beyond aluminum"). The observed properties of gallium and germanium matched those of *eka*-aluminum and *eka*-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.

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Video 9.1.1*: The genius of Mendeleev's periodic table.*

When the chemical properties of an element suggested that it might have been assigned the wrong place in earlier tables, Mendeleev carefully reexamined its atomic mass. He discovered, for example, that the atomic masses previously reported for beryllium, indium, and uranium were incorrect. The atomic mass of indium had originally been reported as 75.6, based on an assumed stoichiometry of InO for its oxide. If this atomic mass were correct, then indium would have to be placed in the middle of the nonmetals, between arsenic (atomic mass 75) and selenium (atomic mass 78). Because elemental indium is a silvery-white

metal, however, Mendeleev postulated that the stoichiometry of its oxide was really In_2O_3 rather than InO. This would mean that indium's atomic mass was actually 113, placing the element between two other metals, cadmium and tin.

Table 9.1.1: Comparison of the Properties Predicted by Mendeleev in 1869 for eka-Aluminum and eka-Silicon with the Properties of Gallium (Discovered in 1875) and Germanium (Discovered in 1886)

Property	*eka*-Aluminum (predicted)	Gallium (observed)	*eka*-Silicon (predicted)	Germanium (observed)
atomic mass	68	69.723	72	72.64
element	metal	metal	dirty-gray metal	gray-white metal
	low mp*	mp = 29.8°C	high mp	mp = 938°C
	ρ = 5.9 g/cm^3	ρ = 5.91 g/cm^3	ρ = 5.5 g/cm^3	ρ = 5.323 g/cm^3
oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
	ρ = 5.5 g/cm^3	ρ = 6.0 g/cm^3	ρ = 4.7 g/cm^3	ρ = 4.25 g/cm^3
chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$
	volatile	mp = 78°C bp* = 201°C	bp < 100°C	bp = 87°C
***mp = melting point; bp = boiling point.**				

One group of elements that absent from Mendeleev's table is the noble gases, all of which were discovered more than 20 years later, between 1894 and 1898, by Sir William Ramsay (1852–1916; Nobel Prize in Chemistry 1904). Initially, Ramsay did not know where to place these elements in the periodic table. Argon, the first to be discovered, had an atomic mass of 40. This was greater than chlorine's and comparable to that of potassium, so Ramsay, using the same kind of reasoning as Mendeleev, decided to place the noble gases between the halogens and the alkali metals.

The Role of the Atomic Number in the Periodic Table

Despite its usefulness, Mendeleev's periodic table was based entirely on empirical observation supported by very little understanding. It was not until 1913, when a young British physicist, H. G. J. Moseley (1887–1915), while analyzing the frequencies of x-rays emitted by the elements, discovered that the underlying foundation of the order of the elements was by the *atomic number*, not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number Z, which is the number of positive charges (protons) in its nucleus. Argon, for example, although having an atomic mass greater than that of potassium (39.9 amu versus 39.1 amu, respectively), was placed *before* potassium in the periodic table. While analyzing the frequencies of the emitted x-rays, Moseley noticed that the atomic number of argon is 18, whereas that of potassium is 19, which indicated that they were indeed placed correctly. Moseley also noticed three gaps in his table of x-ray frequencies, so he predicted the existence of three unknown elements: technetium (Z = 43), discovered in 1937; promethium (Z = 61), discovered in 1945; and rhenium (Z = 75), discovered in 1925.

Note: H. G. J. Moseley (1887–1915)

Moseley left his research work at the University of Oxford to join the British army as a telecommunications officer during World War I. He was killed during the Battle of Gallipoli in Turkey.



Example 9.1.1

Before its discovery in 1999, some theoreticians believed that an element with a Z of 114 existed in nature. Use Mendeleev's reasoning to name element 114 as *eka*-_____; then identify the known element whose chemistry you predict would be most similar to that of element 114.

Given: atomic number

Asked for: name using prefix *eka*-

Strategy:

A. Using the periodic table locate the $n = 7$ row. Identify the location of the unknown element with $Z = 114$; then identify the known element that is directly above this location.
B. Name the unknown element by using the prefix *eka*- before the name of the known element.

Solution:

A The $n = 7$ row can be filled in by assuming the existence of elements with atomic numbers greater than 112, which is underneath mercury (Hg). Counting three boxes to the right gives element 114, which lies directly below lead (Pb). **B** If Mendeleev were alive today, he would call element 114 *eka*-lead.

Exercise 9.1.1

Use Mendeleev's reasoning to name element 112 as *eka*-_____; then identify the known element whose chemistry you predict would be most similar to that of element 112.

Answer: *eka*-mercury

Summary

- The elements in the periodic table are arranged according to their properties, and the periodic table serves as an aid in predicting chemical behavior.

The periodic table arranges the elements according to their electron configurations, such that elements in the same column have

the same valence electron configurations. Periodic variations in size and chemical properties are important factors in dictating the types of chemical reactions the elements undergo and the kinds of chemical compounds they form. The modern periodic table was based on empirical correlations of properties such as atomic mass; early models using limited data noted the existence of **triads** and **octaves** of elements with similar properties. The periodic table achieved its current form through the work of Dimitri Mendeleev and Julius Lothar Meyer, who both focused on the relationship between atomic mass and chemical properties. Meyer arranged the elements by their atomic volume, which today is equivalent to the **molar volume**, defined as molar mass divided by molar density. The correlation with the electronic structure of atoms was made when H. G. J. Moseley showed that the periodic arrangement of the elements was determined by atomic number, not atomic mass.

Contributors and Attributions

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9.2: Metals and Nonmetals and their Ions

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 9.2.1: 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

$$\mathrm{Na^0} \rightarrow \mathrm{Na^+ + e^-} \tag{9.2.1}$$

$$\mathrm{Mg^0} \rightarrow \mathrm{Mg^{2+} + 2\,e^-} \tag{9.2.2}$$

$$\mathrm{Al^0} \rightarrow \mathrm{Al^{3+} + 3\,e^-} \tag{9.2.3}$$

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***:

$$\mathrm{Na_2O\,(s) + H_2O\,(l)} \rightarrow \mathrm{2\,NaOH\,(aq)} \tag{9.2.4}$$

$$\mathrm{CaO\,(s) + H_2O\,(l)} \rightarrow \mathrm{Ca(OH)_2\,(aq)} \tag{9.2.5}$$

Metal oxides exhibit their ***basic*** chemical nature by reacting with ***acids*** to form metal ***salts*** and water:

$$\mathrm{MgO\,(s) + HCl\,(aq)} \rightarrow \mathrm{MgCl_2\,(aq) + H_2O\,(l)} \tag{9.2.6}$$

$$\mathrm{NiO\,(s) + H_2SO_4\,(aq)} \rightarrow \mathrm{NiSO_4\,(aq) + H_2O\,(l)} \tag{9.2.7}$$

Example 9.2.1

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 9.2.2

Would you expect it to be solid, liquid or gas at room temperature?

Solutions

Oxides of metals are characteristically solid at room temperature

Example 9.2.3

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.

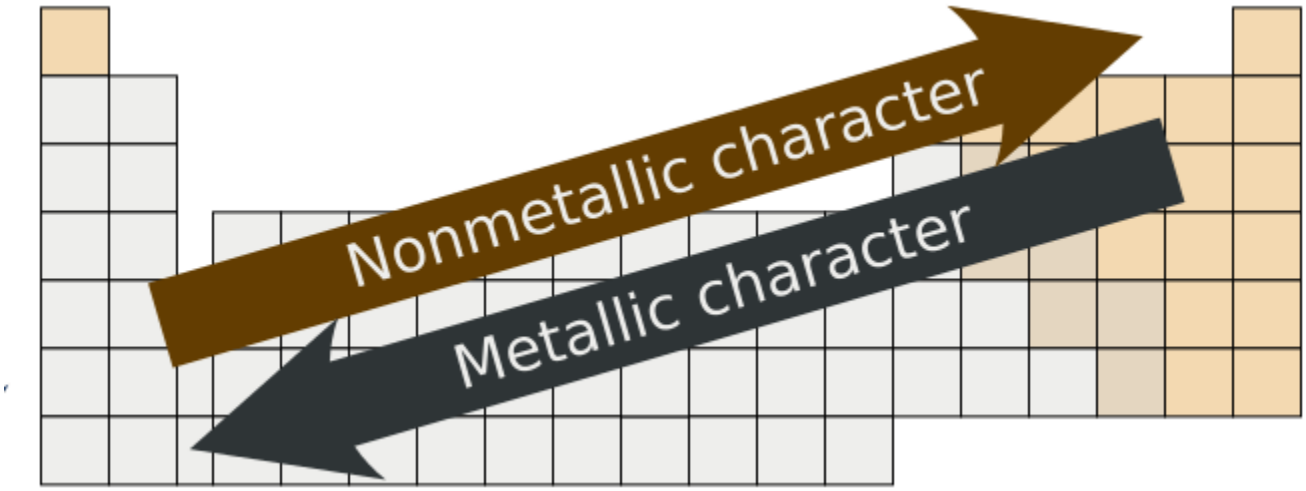
Table 9.2.2: Elements categorized into metals, non-metals and metalloids.

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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9.3: 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. 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 9.3.1 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.

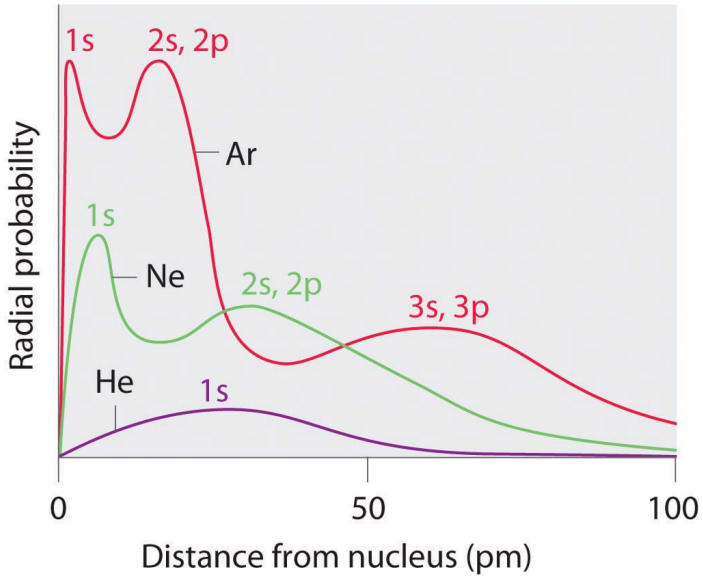


Figure 9.3.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1s electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈8 pm, and the 2s and 2p electrons combine to form another maximum at ≈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 9.3.1 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 9.3.1 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 (part (a) in Figure 9.3.2). Atomic radii are often measured in angstroms (Å), a non-SI unit: 1 Å = 1×10^{-10} m = 100 pm.

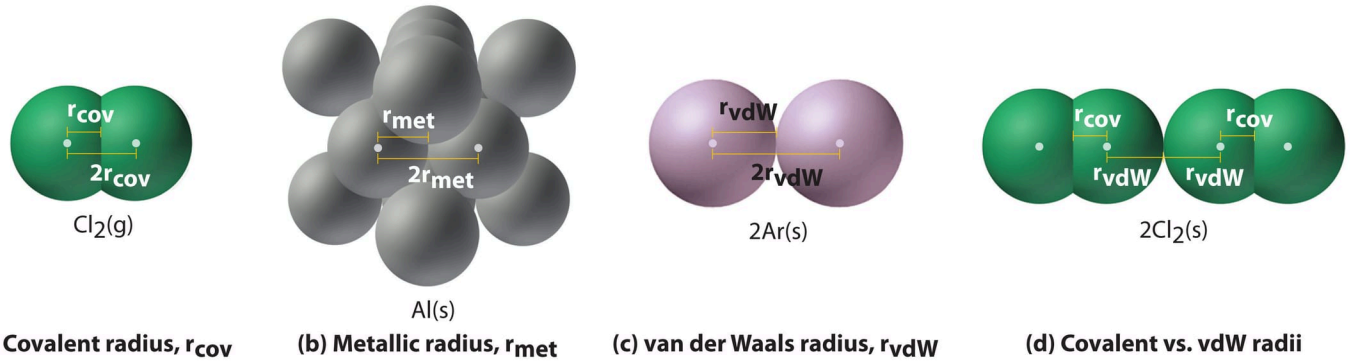


Figure 9.3.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent 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 the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is 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 (part (b) in Figure 9.3.2). 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 (part (c) in Figure 9.3.2). 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 (part (d) in Figure 9.3.2).

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 9.3.3).

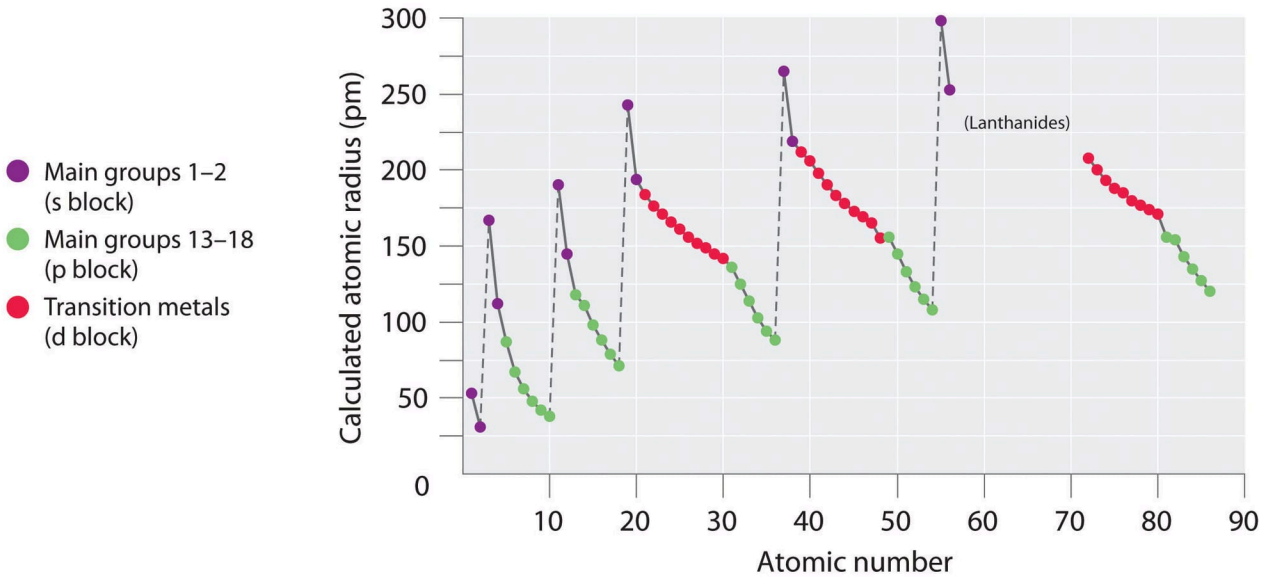


Figure 9.3.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table.

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 9.3.4).

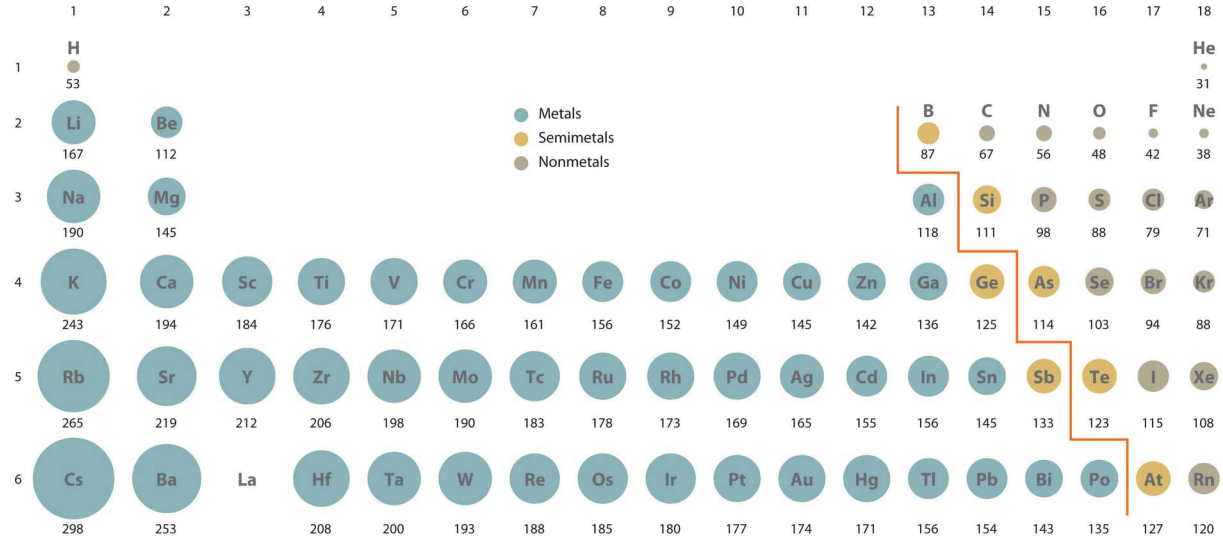


Figure 9.3.4 *Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: http://www.webelements.com. Web Elements is an excellent on line source for looking up atomic properties.*

Note

Atomic radii decrease from left to right across a row and increase from top to bottom down a column.

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.

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.

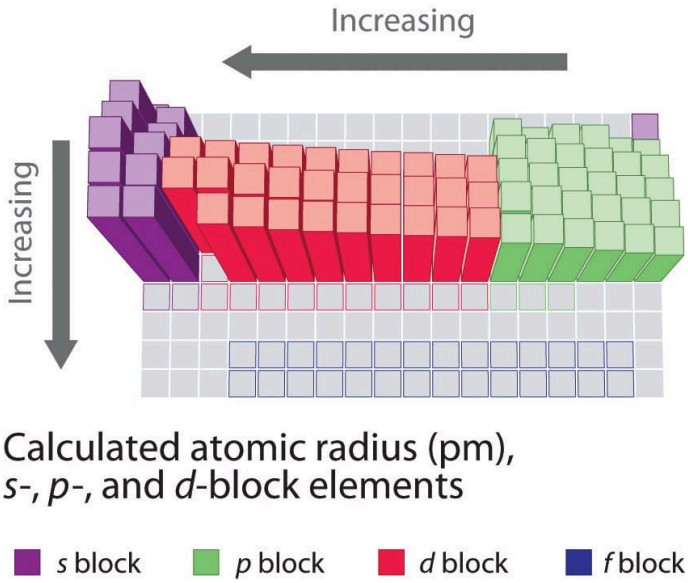


Figure 9.3.5: *The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.*

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.

Note

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 9.3.1

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 9.3.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

Answer: O < S < P < K

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

Atomic Radius: https://youtu.be/ZYKB8SNrGVY

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom (cations) to form a positive ion or when additional electrons attach themselves to neutral atoms (anions) to form a negative one. 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.

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 9.3.6, 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.

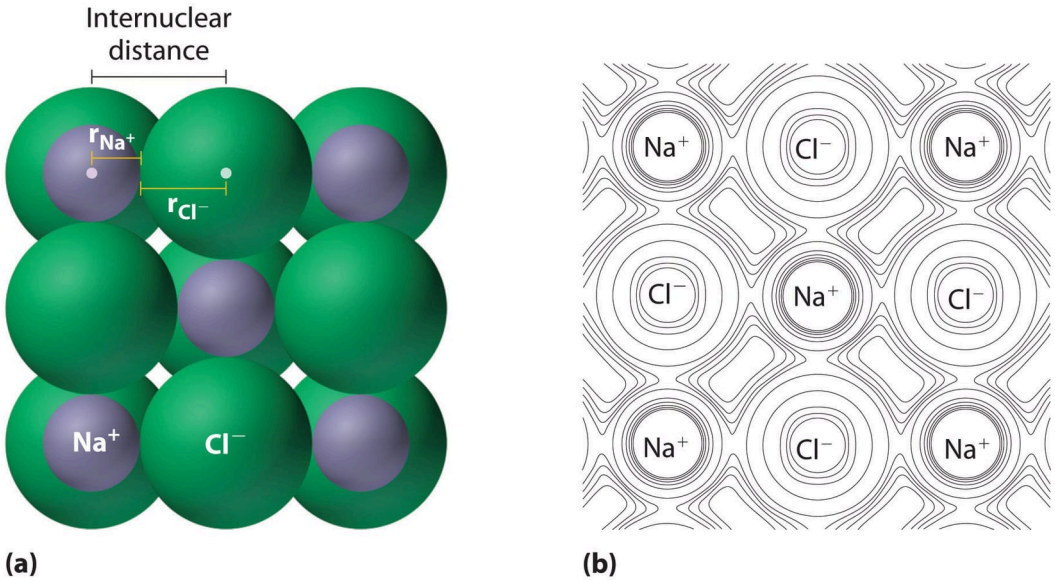


Figure 9.3.6: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for 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^+.

A comparison of ionic radii with atomic radii (Figure 9.3.7) *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 (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 (compare F at 42 pm with F^- at 133 pm).

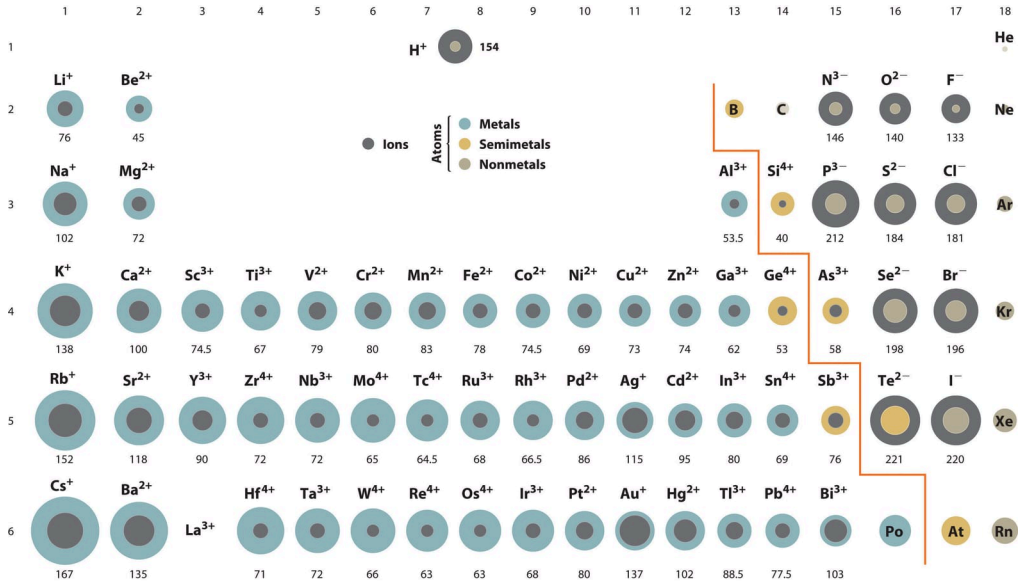


Figure 3.7. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

Note

Cations are **always** smaller than the neutral atom, and anions are **always** larger.

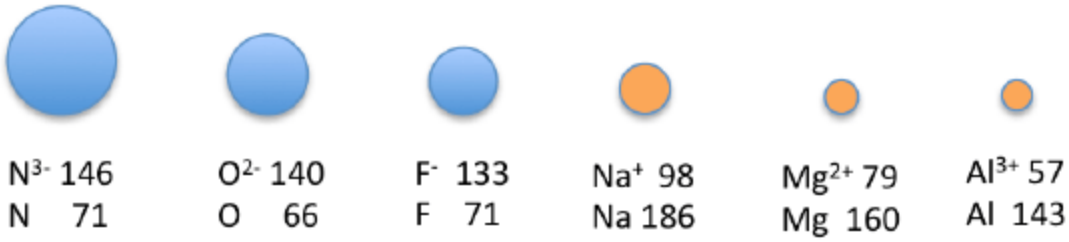
Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table 9.3.1. 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 9.3.1: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6 3s^2$
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 ($1s^2 2s^2 2p^6$) is shown in Table 7.3



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 9.3.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table 9.3.3 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 9.3.2

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 9.3.2

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br^-, Ca^{2+}, Rb^+, and Sr^{2+}.

Answer: $Ca^{2+} < Sr^{2+} < Rb^+ < Br^-$

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.

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9.4: 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. 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

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad \text{energy required=I} \tag{9.4.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 9.4.1. 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):

$$1\ eV/atom = 96.49\ kJ/mol \tag{9.4.2}$$

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:

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad I_1 = \text{1st ionization energy} \tag{9.4.3}$$

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad I_2 = \text{2nd ionization energy} \tag{9.4.4}$$

$$E^+_{(g)} \rightarrow E^{2+}_{(g)} + e^- \qquad I_3 = \text{3rd ionization energy} \tag{9.4.5}$$

Values for the ionization energies of Li and Be listed in Table $9.4.1$ show that successive ionization energies for an element increase steadily; 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.

Note

Successive ionization energies for an element **increase** steadily.

Table $9.4.1$*: Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of*

Reaction	Electronic Transition	I
$Li_{(g)} \rightarrow Li^+_{(g)} + e^-$	$1s^2 2s^1 \rightarrow 1s^2$	I_1 = 520.2

Reaction	Electronic Transition	I
$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^-$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2
$Li^{2+}_{(g)} \rightarrow Li^{3+}_{(g)} + e^-$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0

The most important consequence of the values listed in Table $9.4.1$ 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

$$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^- \tag{9.4.8}$$

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

$$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^- \tag{9.4.9}$$

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 2*s* 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.*

Note

The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.

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 $9.4.2$): 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 $9.4.2$. 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 $9.4.2$: 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	579.4.4	1816.7	2744.8	**11,579.4.4**	—	—	—
***Inner-shell electron**							

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1909.4.4	2914.1	4963.6	6274.0	**21,269.4.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,109.4.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3
***Inner-shell electron**							

Example 9.4.1: 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:

$$E^{3+}_{(g)} \rightarrow E^{4+}_{(g)} + e^- \tag{9.4.10}$$

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 9.4.1: 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: Sr

The first column of data in Table 9.4.2 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.

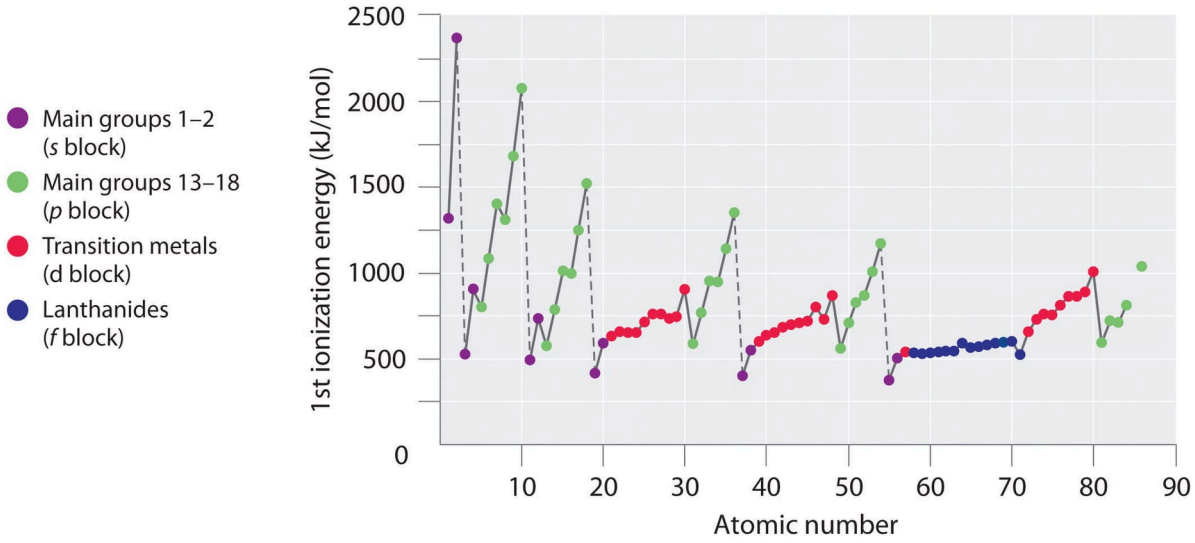


Figure 9.4.1: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). 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. 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.

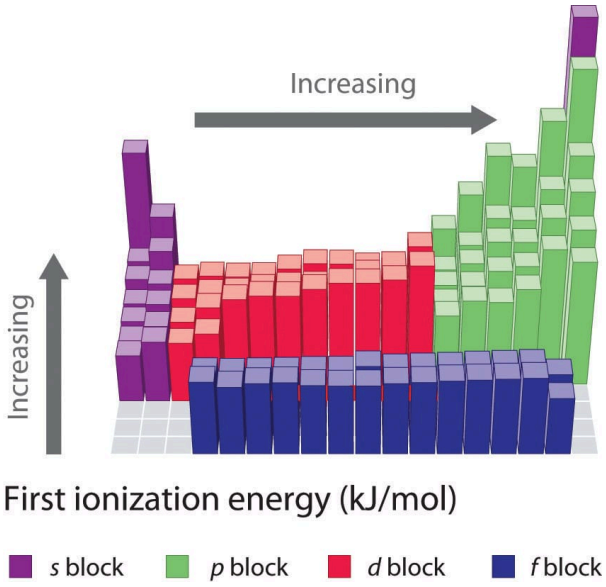


Figure* 9.4.2: *First Ionization Energies of the s-, p-, d-, and f-Block Elements

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 9.4.1 and are presented numerically and graphically in Figure 9.4.2. These figures illustrate three important trends:

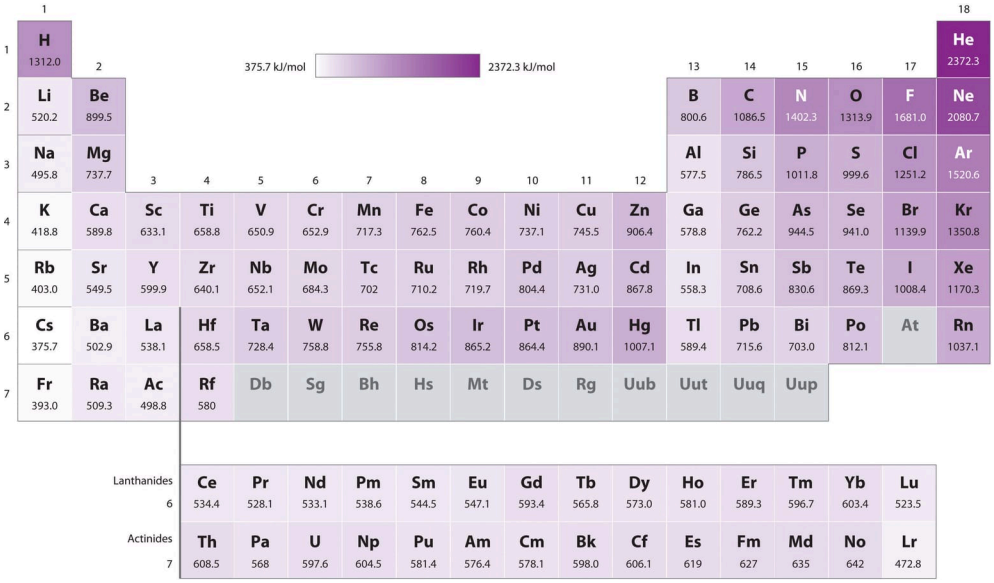
1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the s and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, 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) electron configurations.

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 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).

Note

Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.



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).

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 4*p* subshell, screening the single 4*p* 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 ns, 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 $3d$ orbitals to be slightly lower in energy than the $4s$ orbitals. The $[Ar]3d^2$ electron configuration of Ti^{2+} tells us that the $4s$ electrons of titanium are lost before the $3d$ 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 9.4.2: 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 9.4.2: 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: As

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

Ionization Energy: https://youtu.be/k7j-u02ifzo

Summary

- Generally, the first ionization energy and electronegativity values increase diagonally from the lower left of the periodic table to the upper right, and electron affinities become more negative across a row.

The tendency of an element to lose 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.

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9.5: Electron Affinity

Learning Objectives

- To master the concept of electron affinity as a measure of the energy required to adding 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:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change}{=}EA \tag{9.5.1}$$

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.

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:

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \qquad EA = -346\ kJ/mol \tag{9.5.2}$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$Be_{(g)} + e^- \rightarrow Be^-_{(g)} \qquad EA \geq 0 \tag{9.5.3}$$

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:

$$N_{(g)} + e^- \rightarrow N^-_{(g)} \qquad EA \approx 0 \tag{9.5.4}$$

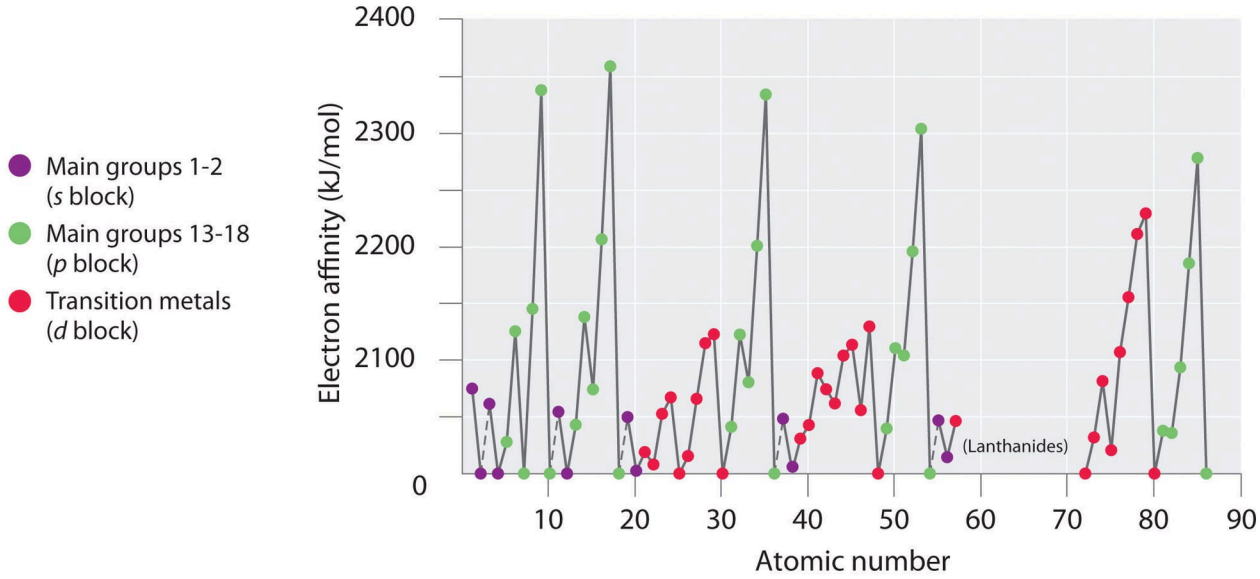


Figure 9.5.1: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table

Note

Generally, electron affinities become more negative across a row of the periodic table.

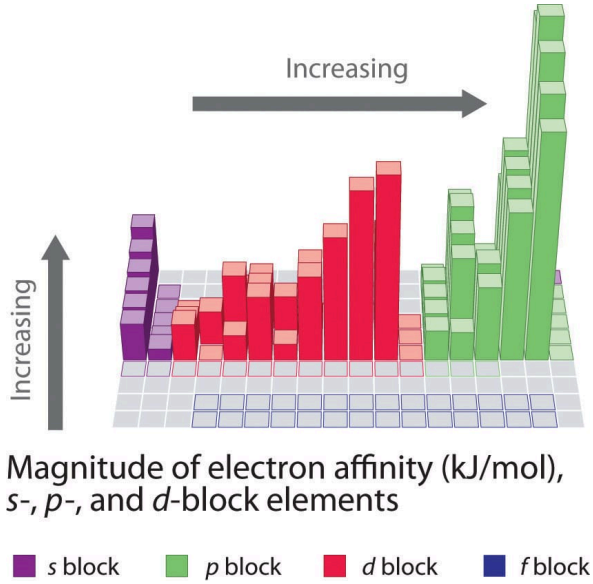
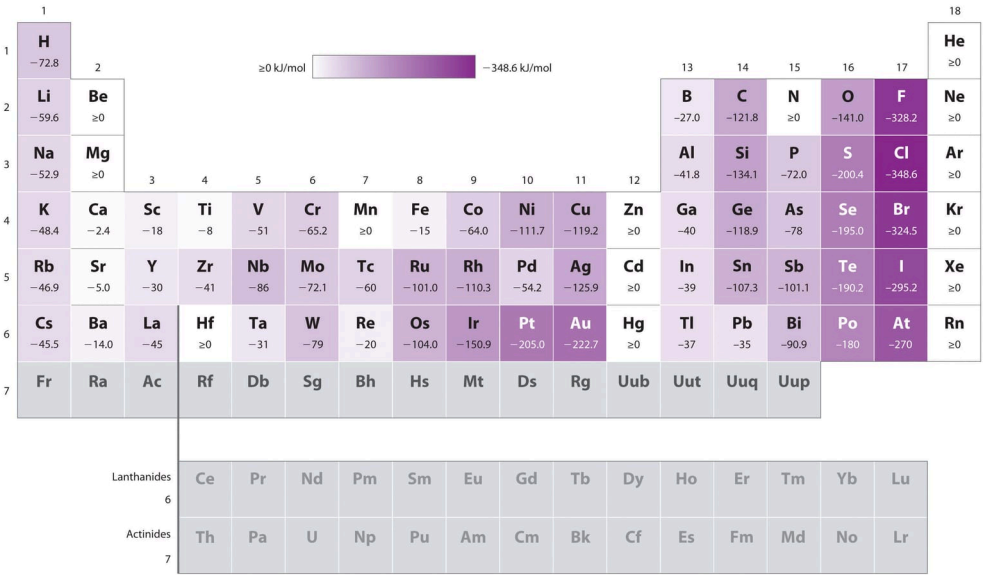


Figure 9.5.2 Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

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. 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.



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).

Note

In general, electron affinities become more negative across a row and less negative down a column.

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA_1 \tag{9.5.5}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change} = EA_2 \tag{9.5.6}$$

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:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{9.5.7}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{9.5.8}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{9.5.9}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

Note

While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.

If energy is required to form both positively charged ions 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 9.5.1: 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 9.5.1: 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: Rb

YouTube Video

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Electron Affinity: https://youtu.be/M5MsRM2Xtds

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.

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9.6: Magnetic Properties

Learning Objectives

- To predict the magnetic properties of atoms and molecules based on their electronic configurations.

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 paramagnetism, and diamagnetism are discussed here.

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 orient in either direction, they exhibit magnetic moments that can align with a magnet. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (that is best understood with molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:

YouTube Video

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Video $9.6.1$***:*** *A chemical demonstration of the paramagnetism of molecular oxygen, as shown by the attraction of liquid oxygen to magnets.*

As shown in Video $9.6.1$, since molecular oxygen (O_2 is paramagnetic, it is attracted to the magnet. In contrast, molecular nitrogen, N_2, has no unpaired electrons and it is diamagnetic (discussed below); it is therefore unaffected by the magnet.

Note

Paramagnetism is a form of magnetism whereby materials are **attracted** by an externally applied magnetic field.

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 as demonstrated with the pyrolytic carbon sheet in Figure 9.6.1.

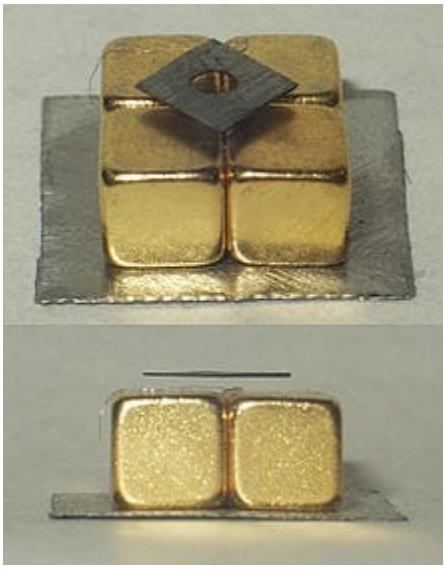


Figure 9.6.1: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

Note

Diamagnetic materials are **repelled** by the applied magnetic field.

Diamagnetism, to a greater or lesser degree, is a property of all materials and always makes a weak contribution to the material's response to a magnetic field. For materials that show some other form of magnetism (such paramagntism), the diamagnetic contribution becomes negligible.

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 electrons unpaired) or diamagnetic (all electrons paired)

YouTube Video

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Determining Magnetic Properties from Orbital Diagrams: https://youtu.be/lun_w5VKD8k

Example 9.6.1: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

Solution

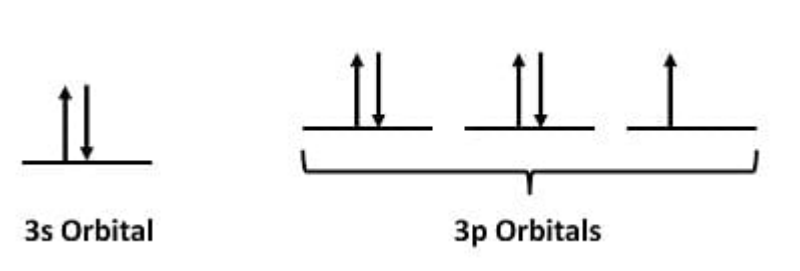
Follow the four steps outlines above.

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 weakly since only one electron is unpaired).

Exercise 9.6.1

Indicate whether boron atoms are paramagnetic or diamagnetic.

Answer:

The B atom has $2s^2 2p^1$ as the electron configuration. Because it has one unpaired electron, it is paramagnetic.

Example 9.6.2: Zinc Atoms

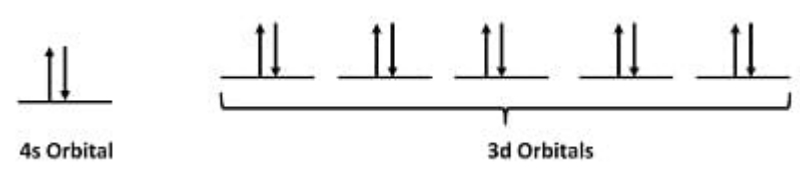
Are zinc atoms paramagnetic or diamagnetic?

Solution

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.

Exercise 9.6.2

Indicate whether F^- ions are paramagnetic or diamagnetic.

Answer

The F^- ion has $2s^2 2p^6$ has the electron configuration. Because it has no unpaired electrons, it is diamagnetic.

Problems

1. How many unpaired electrons are found in oxygen atoms ?
2. How many unpaired electrons are found in bromine atoms?
3. Indicate whether Fe^{2+} ions are paramagnetic or diamagnetic.

Answers

1. The O atom has $2s^2 2p^4$ as the electron configuration. Therefore, O has 2 unpaired electrons.
2. The Br atom has $4s^2 3d^{10} 4p^5$ as the electron configuration. Therefore, Br has 1 unpaired electron.
3. The Fe^{2+} ion has $3d^6$ has the electron configuration. Because it has 4 unpaired electrons, it is paramagnetic.

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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9.7: Periodic Properties of the Elements

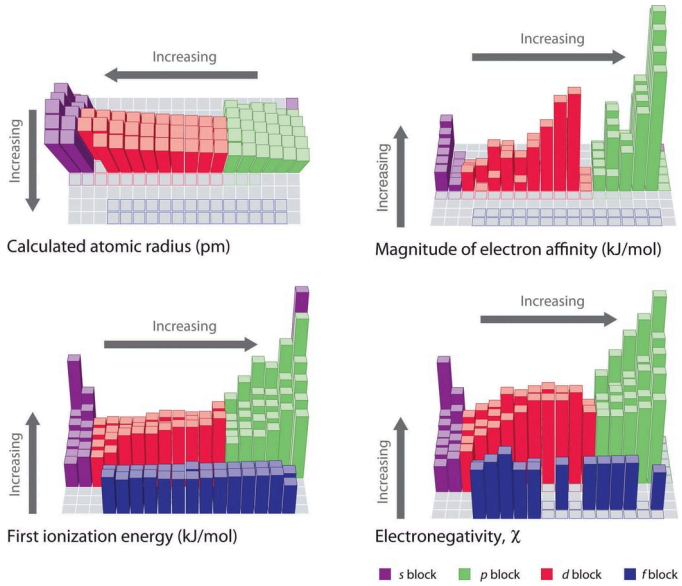


Figure 9.7.1 Summary of Major Periodic Trends. The general trends for the first ionization energy, electron affinity, and electronegativity are opposite to the general trend for covalent atomic radius.

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10: CHEMICAL BONDING I: BASIC CONCEPTS

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

We defined a chemical bond as the force that holds atoms together in a chemical compound. We also introduced two idealized types of bonding: **covalent bonding**, in which electrons are shared between atoms in a molecule or polyatomic ion, and **ionic bonding**, in which positively and negatively charged ions are held together by electrostatic forces. The concepts of covalent and ionic bonding were developed to explain the properties of different kinds of chemical substances.

10.1: Lewis Theory: An Overview
10.2: Covalent Bonding: An Introduction
10.3: Polar Covalent Bonds and Electrostatic Potential Maps
10.4: Writing Lewis Structures
10.5: Resonance
10.6: Exceptions to the Octet Rule
10.7: Shapes of Molecules
10.9: Bond Energies

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10.1: Lewis Theory: An Overview

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.

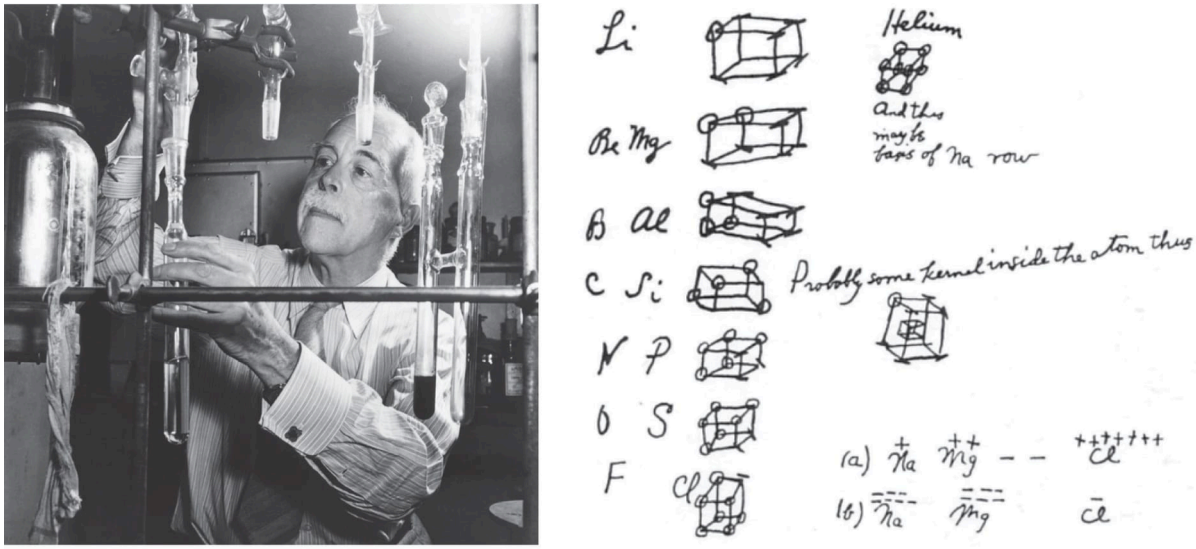


Figure 10.1.1: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Symbols

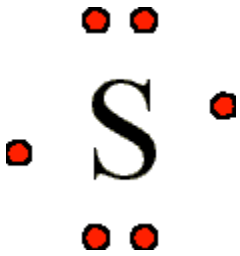
At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

Note

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:

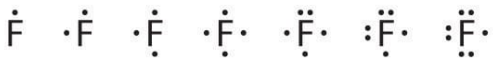


Figure 10.1.2.

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 10.1.2. 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	$[He]2s^2 2p^1$	·B·
C	$[He]2s^2 2p^2$	·C·
N	$[He]2s^2 2p^3$	·N:
O	$[He]2s^2 2p^4$	:O:
F	$[He]2s^2 2p^5$	:F:
Ne	$[He]2s^2 2p^6$	:Ne:

Figure 10.1.2: Lewis Dot Symbols for the Elements in Period 2

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.

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., CH_4

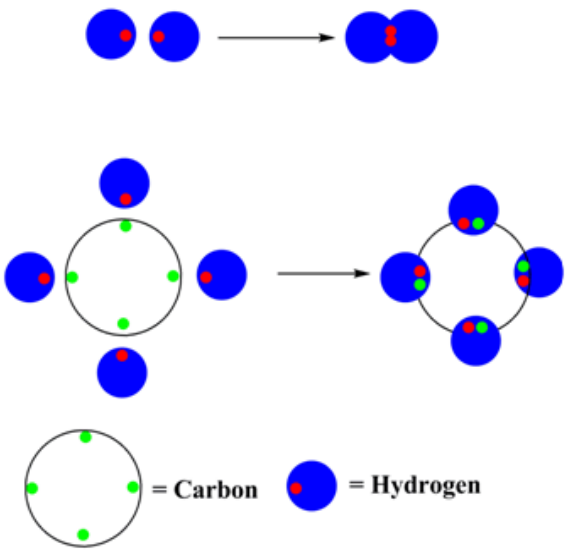


Figure 1: Bonding in H_2 and methane (CH_4)

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.

Note

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 1: Salt

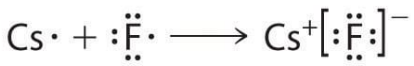
The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat 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.

Note

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.

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Lewis Theory of Bonding: https://youtu.be/TZ6C5_k-SPs

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

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10.2: Covalent Bonding: An Introduction

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

Note

A chemical bond formed by sharing a pair of electrons is called a covalent bond

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 $10.2.1$):

- 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.

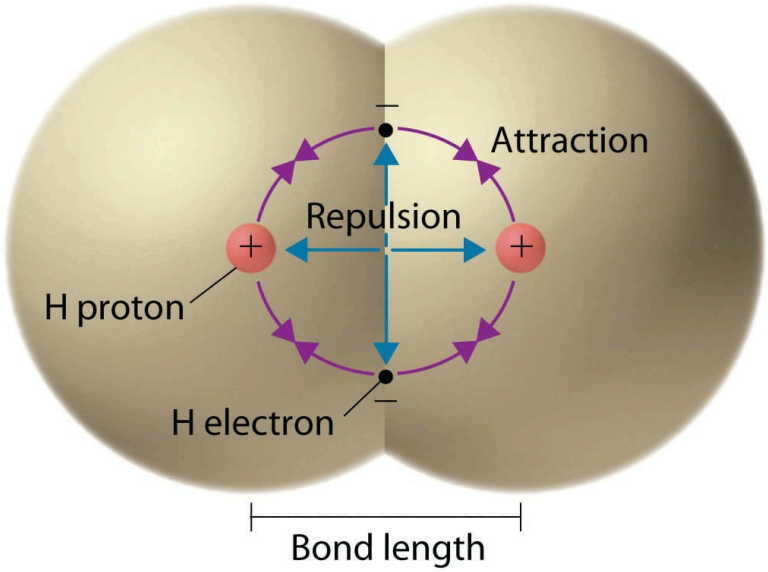


Figure 10.2.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 10.2.2) 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 Figure 10.2.2 and Figure 8.1, 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.

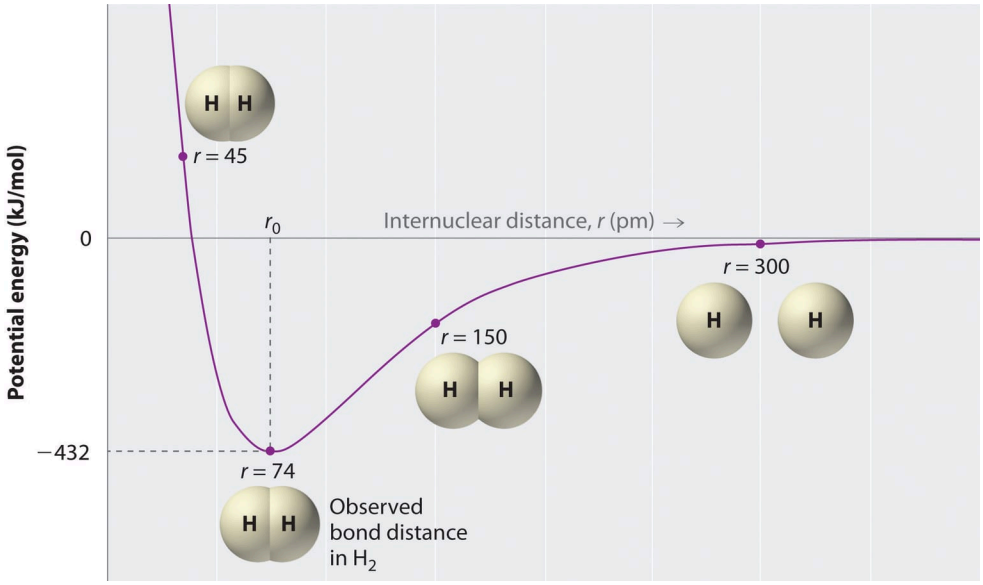


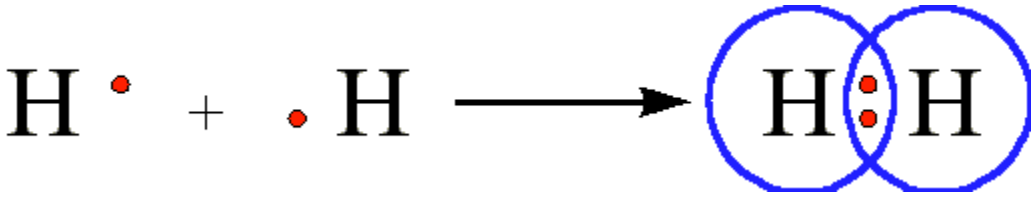
Figure 10.2.2: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

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.

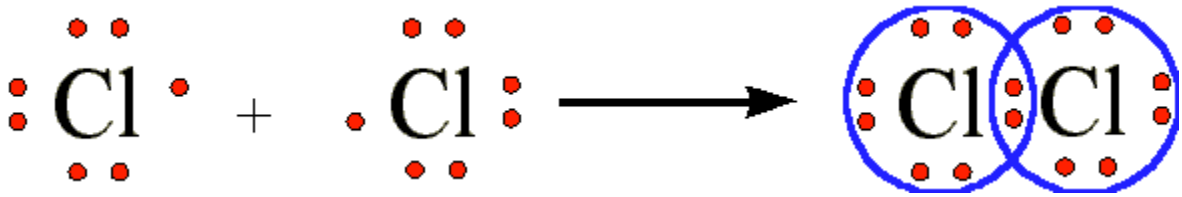
Lewis Structures

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:



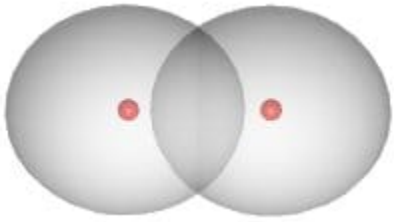
The ***shared pair*** of electrons provides ***each*** hydrogen atom with two electrons in its valence shell (the 1s) orbital. In a sense, each hydrogen atoms has the electron configuration of the noble gas helium (the octet rule). When two chlorine atoms covalently bond to form Cl_2, the following sharing of electrons occurs:



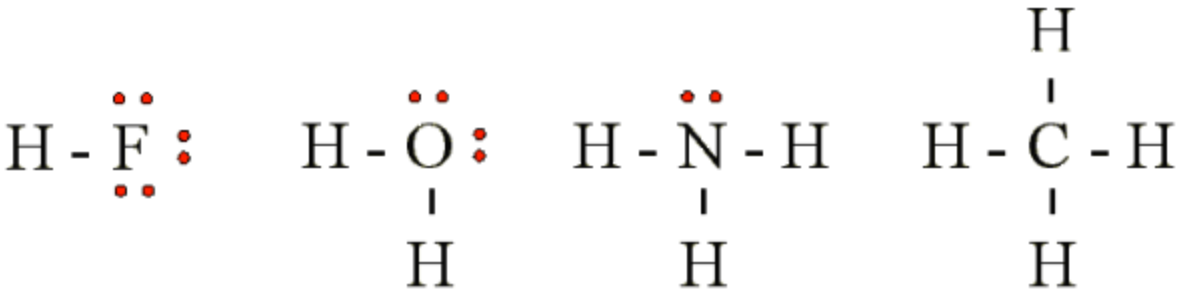
Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon. In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:



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***



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:

Element	Group	Valence electrons	Bonds needed to form valence octet
F	17	7	1
O	16	6	2
N	15	5	3
C	14	4	4

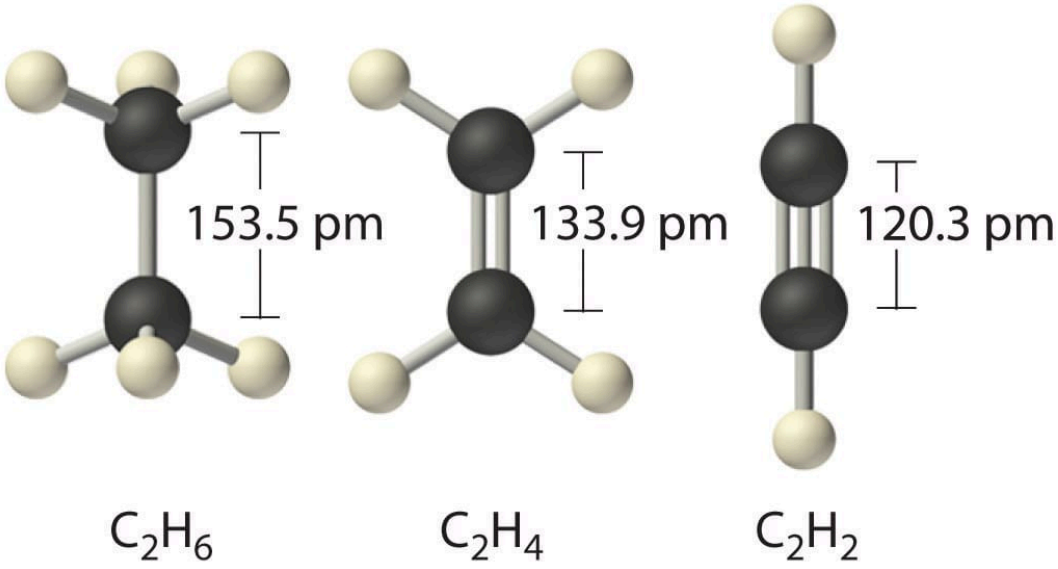
YouTube Video

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View this YouTube Video online

Lewis Structure of Molecules: https://youtu.be/xWiFCqA9Ur0

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 10.2.1, 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 10.2.1: 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

Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)
$H_2N–NH_2$	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); http://cccbdb.nist.gov.

Note

As a general rule, the distance between bonded atoms decreases as the number of shared electron pairs increases

YouTube Video

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Bond Lengths: https://youtu.be/9xn04FNkq9I

The Relationship between Bond Order & Bond Energy

As shown in Table 10.2.1, 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 10.2.2: 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

Single Bonds								Multiple Bonds	
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 10.2.2 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 10.2.1).
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 10.2.1. 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\[\ce{Cl\bond{-}Cl > Br\bond{-}Br > F\bond{-}F > I–I}\] Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

Note

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.

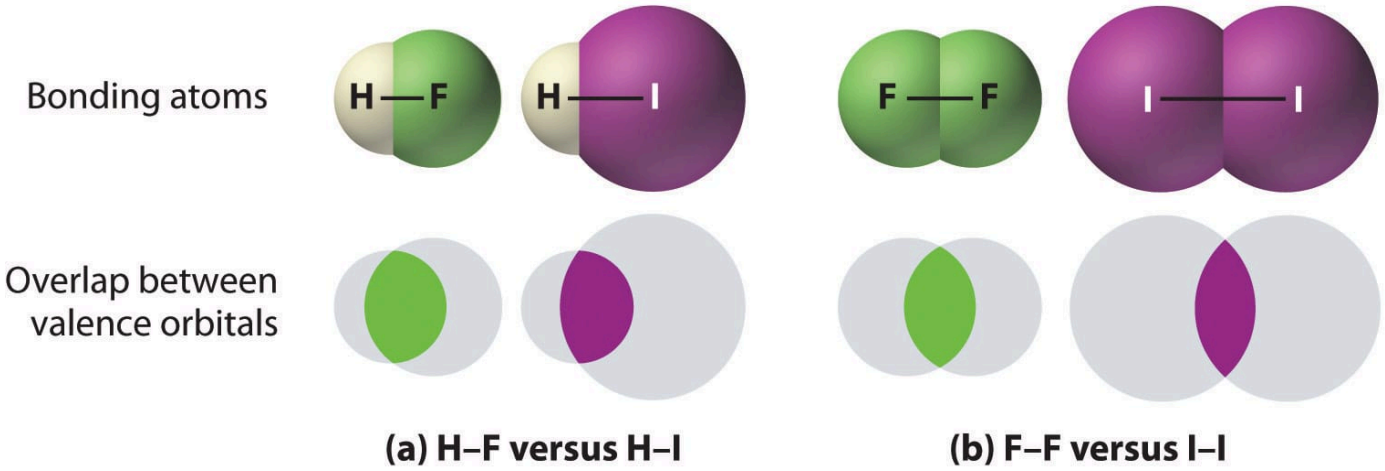


Figure 10.2.1 The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) 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.

Note

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 10.2.3); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 10.2.2 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 10.2.3: 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 ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \tag{10.2.1}$$

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:

$$CH_3(CH_2)_5CH_{3(l)} + 11O_{2(g)} \rightarrow 7CO_{2(g)} + 8H_2O_{(g)} \tag{10.2.2}$$

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:

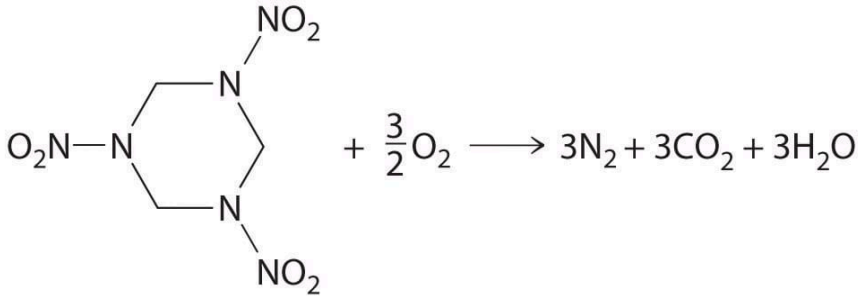
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

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).

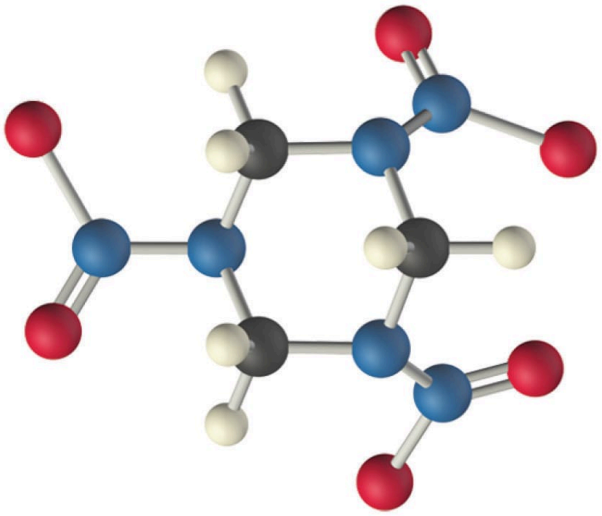
If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481 \ \ 7kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules 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 10.2.1

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 10.2.2 to estimate the ΔH_{rxn} per mole of RDX.



RDX



RDX

Given: chemical reaction, structure of reactant, and Table $10.2.2$.

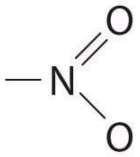
Asked for: ΔH_{rxn} per mole

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)	
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 8.3.1, we have

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \tag{10.2.3}$$

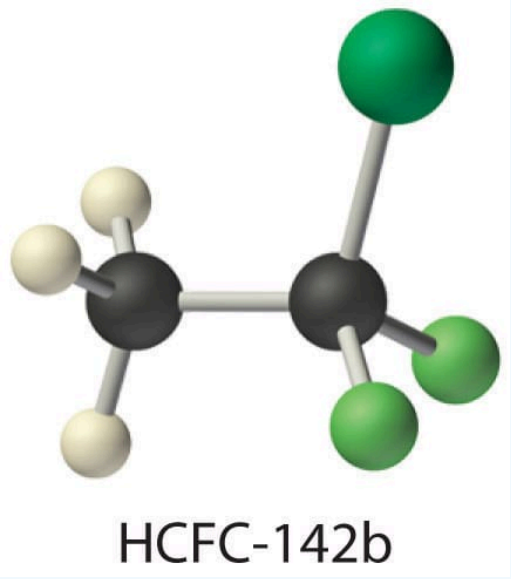
$$= 7962\ kJ/mol - 10,374\ kJ/mol \tag{10.2.4}$$

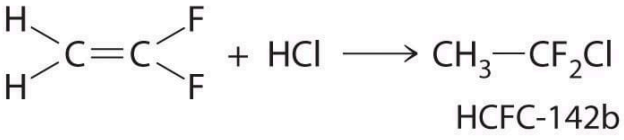
\[=–2412 \;kJ/mol]

Thus this reaction is also highly exothermic.

Exercise 10.2.1

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:





Use tabulated bond energies to calculate ΔH_{rxn}.

Answer: –54 kJ/mol

YouTube Video

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Bond Energies: https://youtu.be/Prc6fbLXi5M

Summary

- The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms.

Formal charge on an atom:

Label '8.3.1' multiply defined

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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10.3: Polar Covalent Bonds and Electrostatic Potential Maps

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 shared electron pairs 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. We 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 (compare Figure $10.3.2$ and Figure $10.3.2$). 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.

Note

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 that is will be *highly electronegative* has:

- a large (negative) electron affinity
- a high ionization energy (always endothermic, or positive for neutral atoms)

and will

- attract electrons from other atoms
- 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.

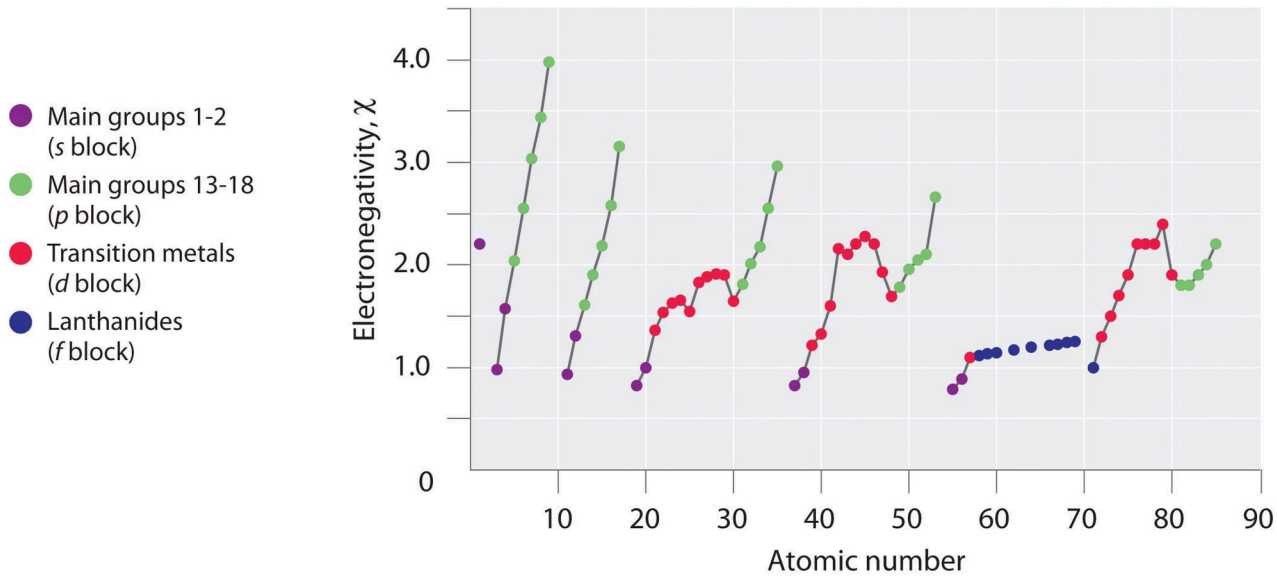


Figure 10.3.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

Periodic variations in Pauling's electronegativity values are illustrated in Figure 10.3.1 and Figure 10.3.2. 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).

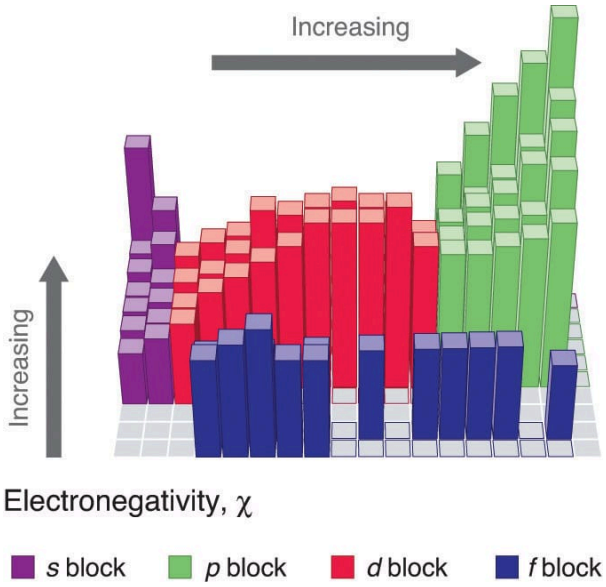
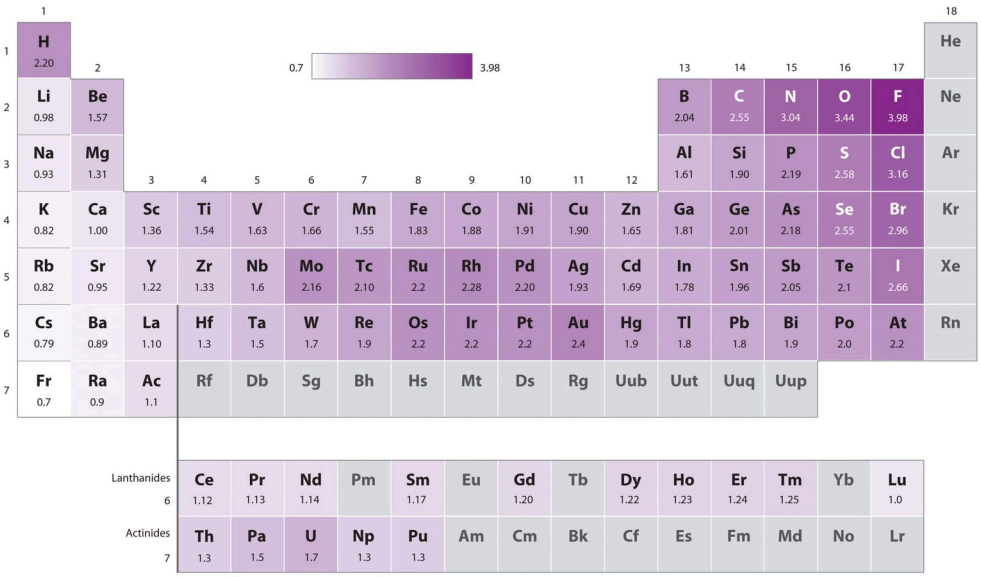


Figure 10.3.2***:*** *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the*

Chemical Bond, 3rd ed. (1960).

Linus Pauling (1901-1994)

Pauling won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962. 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 denied a high school degree because of his refusal to take a civics class.



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 electronegativity scale).

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 ($\chi \geq 2.2$) 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 **semimetals** (or metalloids), 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 $10.3.3$ shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

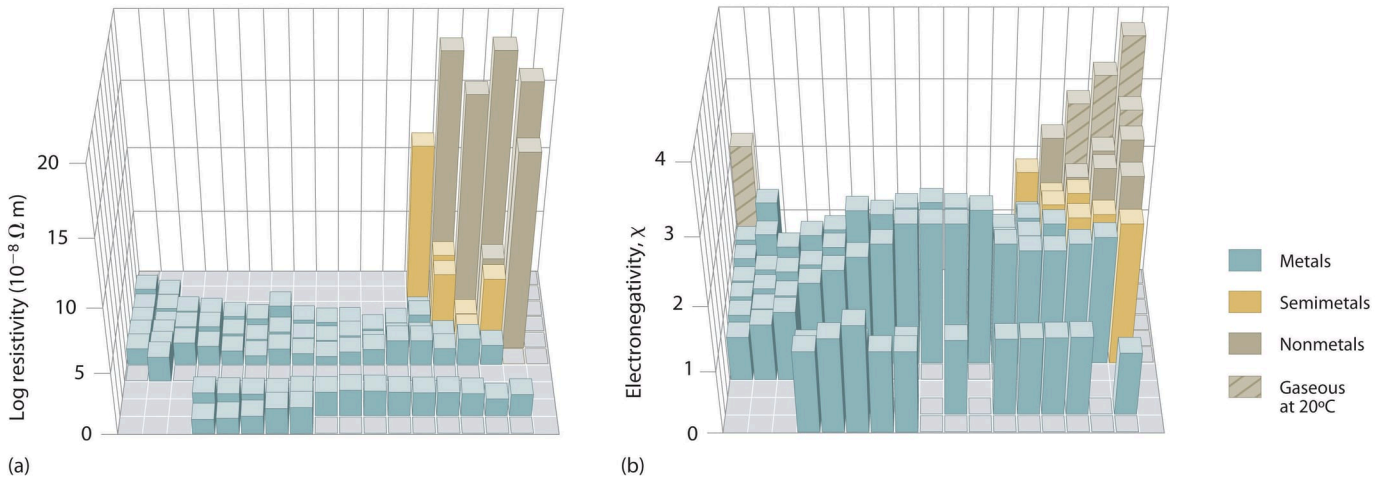


Figure 10.3.3: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (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).

Note

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states 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 10.3.1

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 semimetal.

Given: four elements

Asked for: order by increasing electronegativity and classification

<p">**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 semimetal according to its location about the diagonal belt of semimetals running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 10.3.2). 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 semimetals 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 semimetal, and Se and Cl are nonmetals.

</p">

Exercise 10.3.1

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 semimetal.

Answer: Rb < Zr < Ge < N < O; metals (Rb, Zr); semimetal (Ge); nonmetal (N, O)

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

Electronegativity: https://youtu.be/3Pe0iShCdhM

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 $10.3.4$ 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.

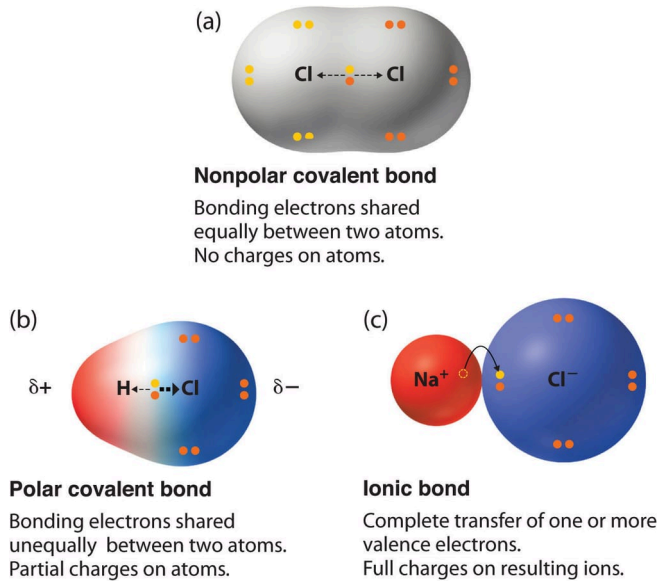


Figure 10.3.4: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely 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:

$$\underset{\delta^+}{A} - \underset{\delta^-}{B} \qquad \begin{matrix} less\ electronegative \\ \\ \end{matrix} \qquad \begin{matrix} more\ electronegative \\ \\ \end{matrix}$$

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 $\chi_{Na} = 0.93$ (see Figure 10.3.2). 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.

Note

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 as a Measure of Bond Polarity

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:

$$\mu = Qr \tag{10.3.1}$$

where Q is measured in coulombs (C) and *r* in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot \cdot m \tag{10.3.2}$$

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 $10.3.2$).

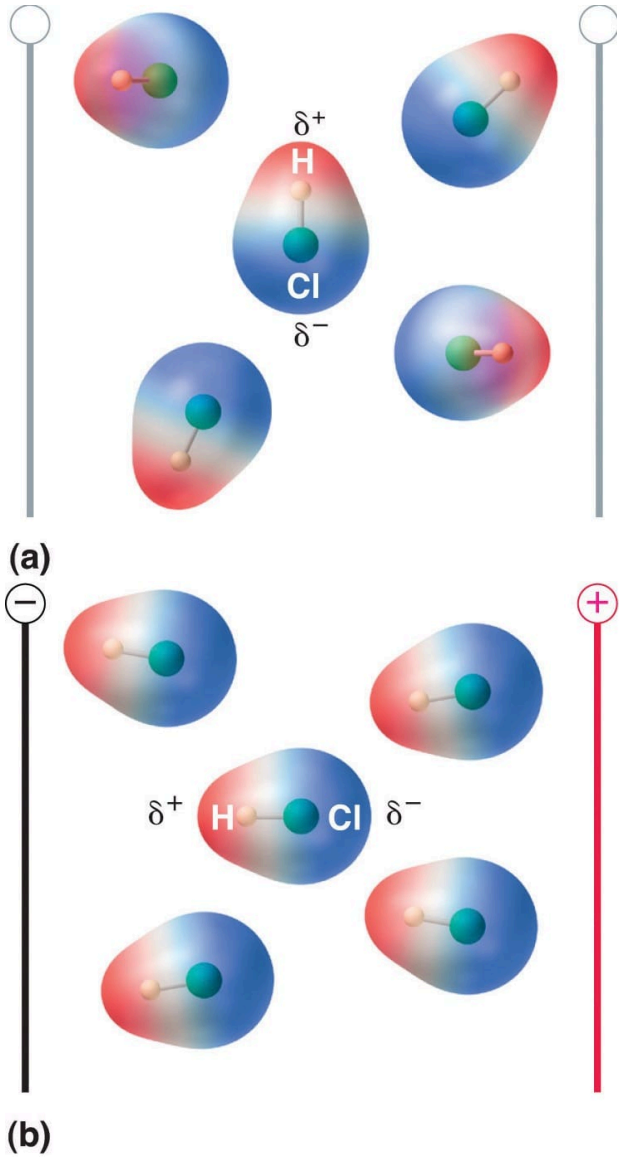


Figure 10.3.5: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive 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 10.3.2 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

$$Q = \frac{\mu}{r} = 1.109 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{127.8\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 2.901 \times 10^{-20}\ C \tag{10.3.3}$$

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.

$$\frac{2.901 \times 10^{-20}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} = 0.1811\ e^- \tag{10.3.4}$$

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

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

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 10.3.6 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 10.3.6 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 11.

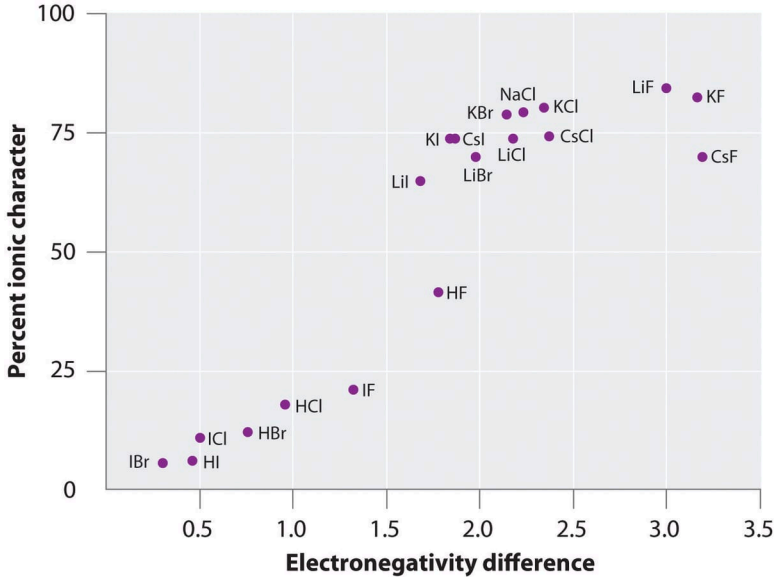


Figure 10.3.6: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 10.3.2

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 10.3.2.

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

$$Q = \frac{\mu}{r} = 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{pm}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 1.272 \times 10^{-19}\ C \tag{10.3.5}$$

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):

$$\%\ ionic\ character = \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) = 79.39\% \simeq 79\% \tag{10.3.6}$$

Exercise 10.3.2

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: 55.5%

YouTube Video

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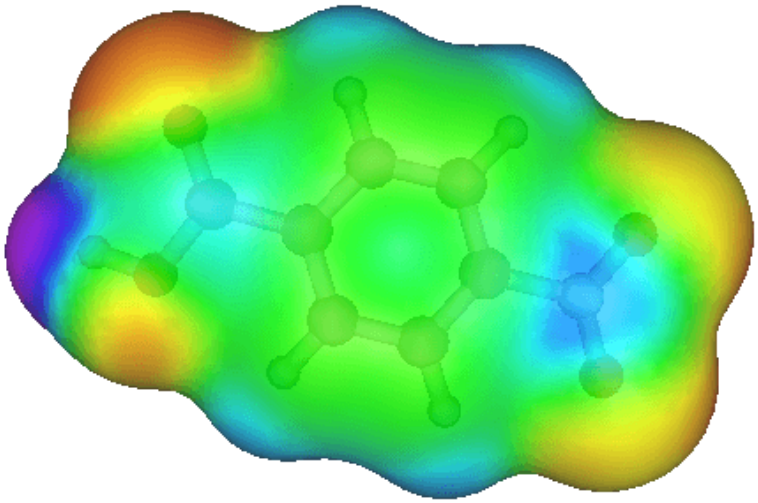
View this YouTube Video online

Dipole Intermolecular Force: https://youtu.be/ACq_95SIBck

Electrostatic Potential Maps

Electrostatic potential maps convey information about the charge distribution of a molecule because of the properties of the nucleus and nature of electrostatic potential energy. A region of higher than average electrostatic potential energy indicates the presence of a stronger positive charge or a weaker negative charger. Given the positive charge of the nuclei, the higher potential

energy value indicates the absence of negative charges (less screening of the nuclei), which would mean that there are fewer electrons in this region. The converse is also true with a low electrostatic potential indicateing an abundance of electrons. This property of electrostatic potentials can be extrapolated to molecules as well.



Note: Constructing a Electrostatic Potential Map

The first step involved in creating an electrostatic potential map is collecting a very specific type of data: electrostatic potential energy. An advanced computer program calculates the electrostatic potential energy at a set distance from the nuclei of the molecule. Electrostatic potential energy is fundamentally a measure of the strength of the nearby charges, nuclei and electrons, at a particular position. To accurately analyze the charge distribution of a molecule, a very large quantity of electrostatic potential energy values must be calculated. The best way to convey this data is to visually represent it, as in an electrostatic potential map. A computer program then imposes the calculated data onto an electron density model of the molecule. To make the electrostatic potential energy data easy to interpret, a color spectrum, with red as the lowest electrostatic potential energy value and blue as the highest, is employed to convey the varying intensities of the electrostatic potential energy values.

The most important thing to consider when analyzing an electrostatic potential map is the charge distribution. The relative distributions of electrons will allow you to deduce everything you need to know from these maps. Recall the relationship between electrostatic potential and charge distribution. Areas of low potential, red, are characterized by an abundance of electrons. Areas of high potential, blue, are characterized by a relative absence of electrons. Oxygen has a higher electronegativity value than sulfur (Table A2), hence. oxygen atoms would have a higher electron density around them than sulfur atoms. Thus the spherical region that corresponds to an oxygen atom would have a red portion on it. Now note that there are two oxygen atoms in sulfur dioxide (Figure 10.3.7). There are two sphere shaped objects that have red regions. These areas correspond to the location of the oxygen atoms. The blue tainted sphere at the top corresponds to the location of the sulfur atom.

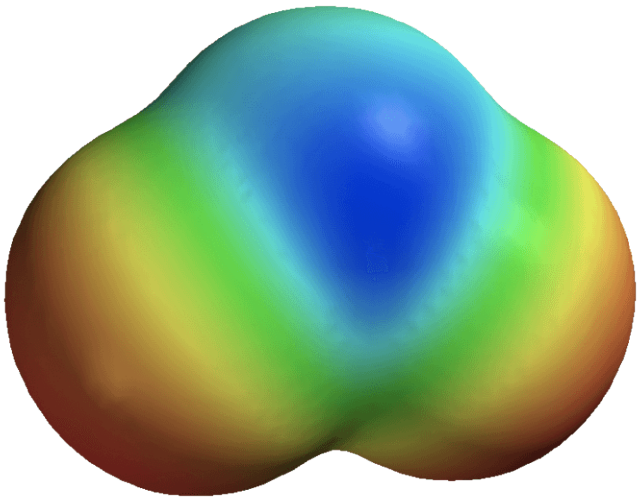


Figure 10.3.7. The electrostatic diagram of Sulfur Dioxide (SO_2). Which parts of this diagram correlate to the respective atomic components? Red indicates the lowest electrostatic potential energy, and blue indicates the highest electrostatic potential energy. Intermediary colors represent intermediary electrostatic potentials.

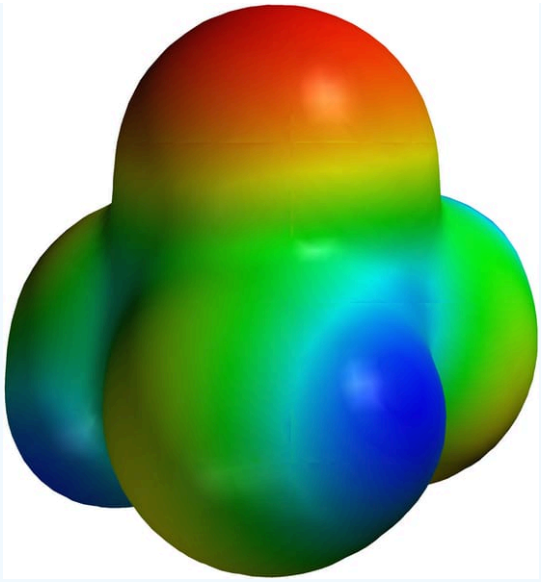
Note

A high electrostatic potential indicates the relative **absence** of electrons and a low electrostatic potential indicates an **abundance** of electrons

Electrostatic potential maps can also be used to determine the nature of the molecules chemical bond. Consider SO_2 in Figure 10.3.7, there is a great deal of intermediary potential energy, the non red or blue regions, in this diagram. This indicates that the electronegativity difference is not very great. In a molecule with a great electronegativity difference, charge is very polarized, and there are significant differences in electron density in different regions of the molecule. This great electronegativity difference leads to regions that are almost entirely red and almost entirely blue. Greater regions of intermediary potential, yellow and green, and smaller or no regions of extreme potential, red and blue, are key indicators of a smaller electronegativity difference. Note that the electronegativity difference is a key determinant in the nature of a chemical bond.

Example 10.3.3

The following electrostatic potential map of phosphoric acid $\backslash \mathrm{H}_3PO_4$. What regions correspond to atoms of oxygen, hydrogen, and phosphorous respectively?



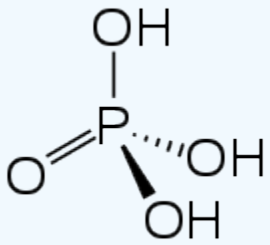
Solution

You do not need to know the molecular structure to answer this question. You do need to know the relative electronegative values of these atoms (Table A4).

- Oxygen has the greatest electronegative value,
- Phosphorous the second most, and
- Hydrogen has the smallest electronegative value.

Simply by knowing this, you can deduce that oxygen would be affiliated with the red region or redish regions of the diagram, and hydrogen would be affiliated with the blue region. Phosphorous would fall in between these two extremes, in the green region.

Here is the molecular diagram of phosphoric acid:



Summary

- Bond polarity and ionic character increase with an increasing difference in electronegativity.

Dipole moment

Label '10.3.2' multiply defined

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.

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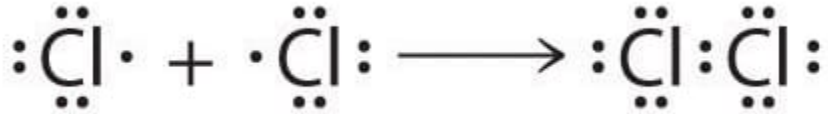
10.4: Writing Lewis Structures

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

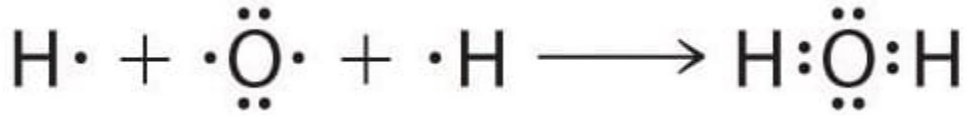
Using Lewis Dot Symbols to Describe Covalent Bonding

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.

Note

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

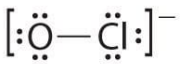
1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each 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:



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.

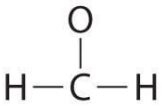
The CH_2O Molecule

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:



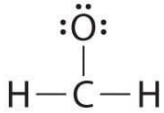
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

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.

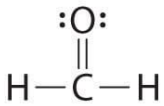
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



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:



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 10.4.1

Write the Lewis electron structure for each species.

1. NCl_3
2. S_2^{2-}
3. NOCl

Given: chemical species

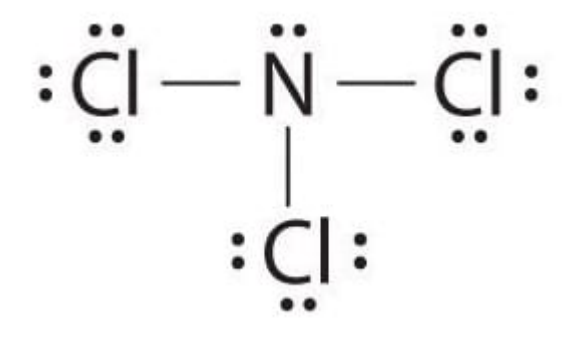
Asked for: Lewis electron structures

Strategy:

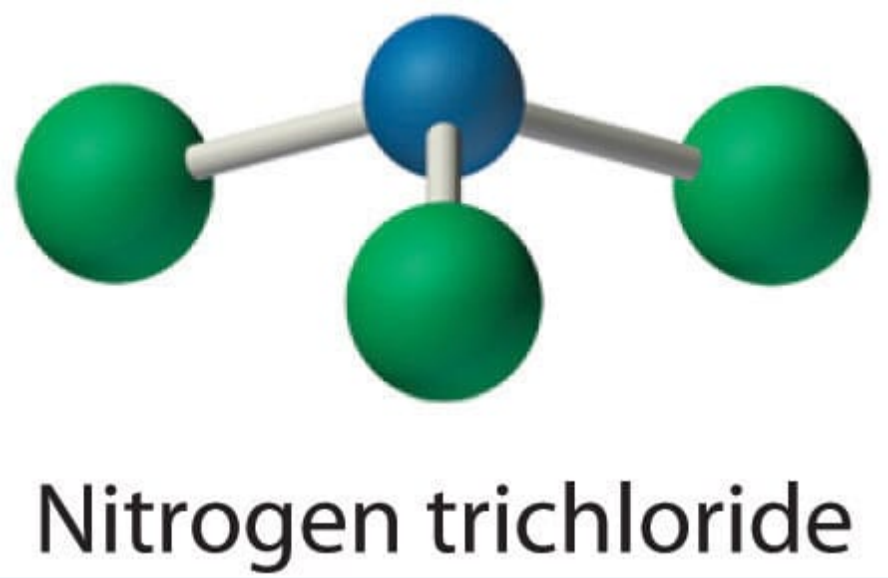
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

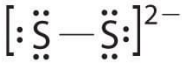
1. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl 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:



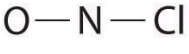
Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



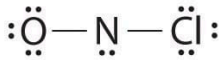
2. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the –2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



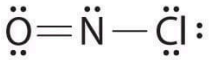
3. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



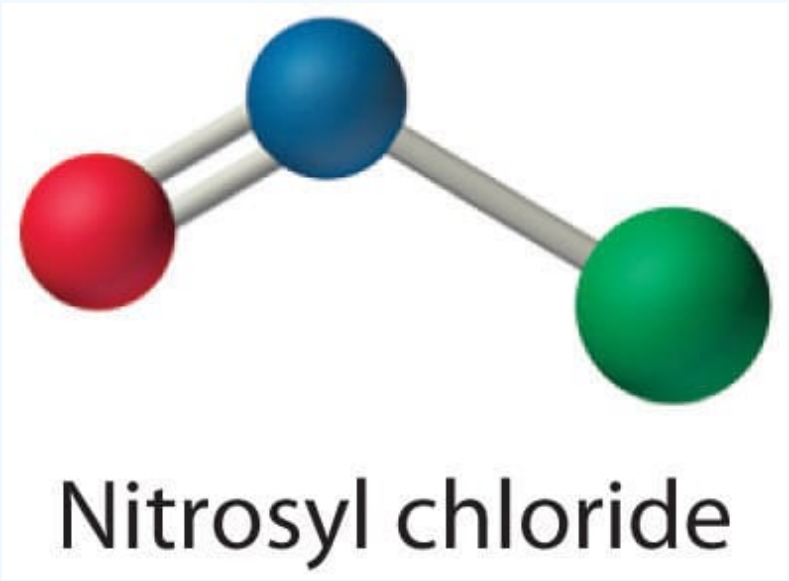
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



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:



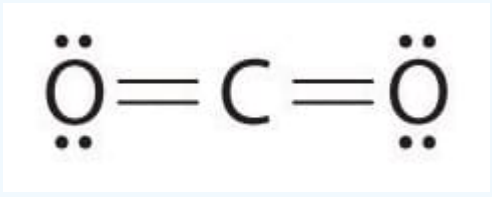
All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



Exercise 10.4.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

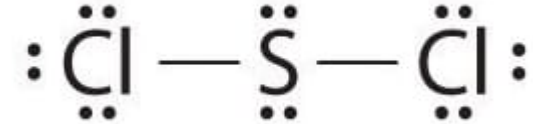
Answer

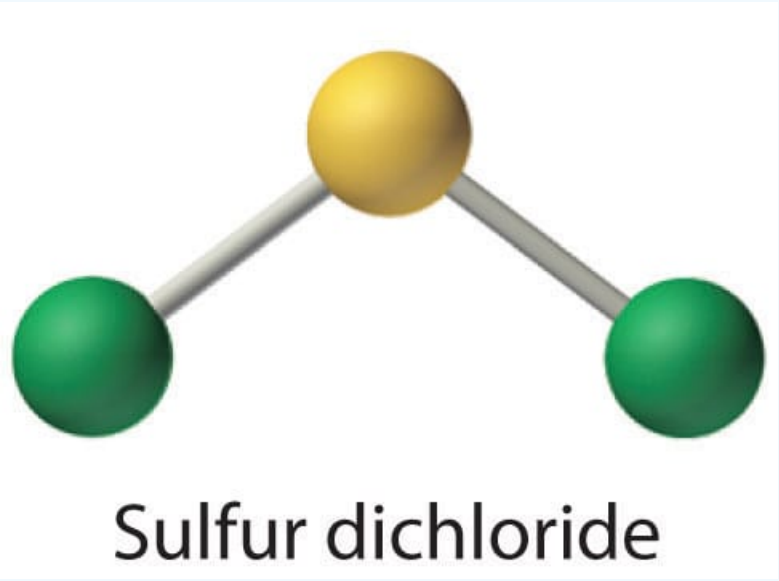
1. 



Carbon dioxide

2.





Sulfur dichloride

YouTube Video

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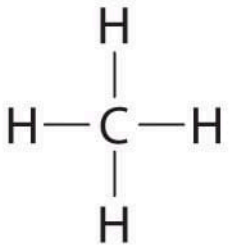
View this YouTube Video online

Lewis Structure of Molecules: https://youtu.be/xWiFCqA9Ur0

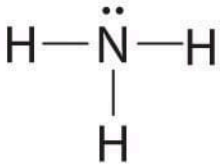
Using Lewis Electron Structures to Explain Stoichiometry

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

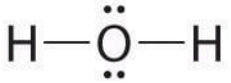
one; for the elements of Group 16 (the chalcogens), it is two; for Group 15 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



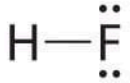
Group 14



Group 15

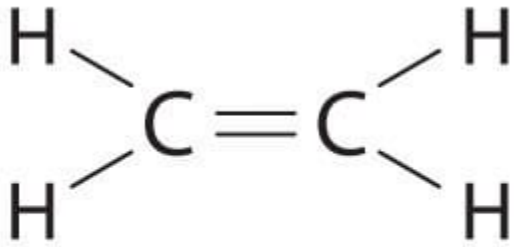


Group 16



Group 17

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.

Note

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 $10.4.3$). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

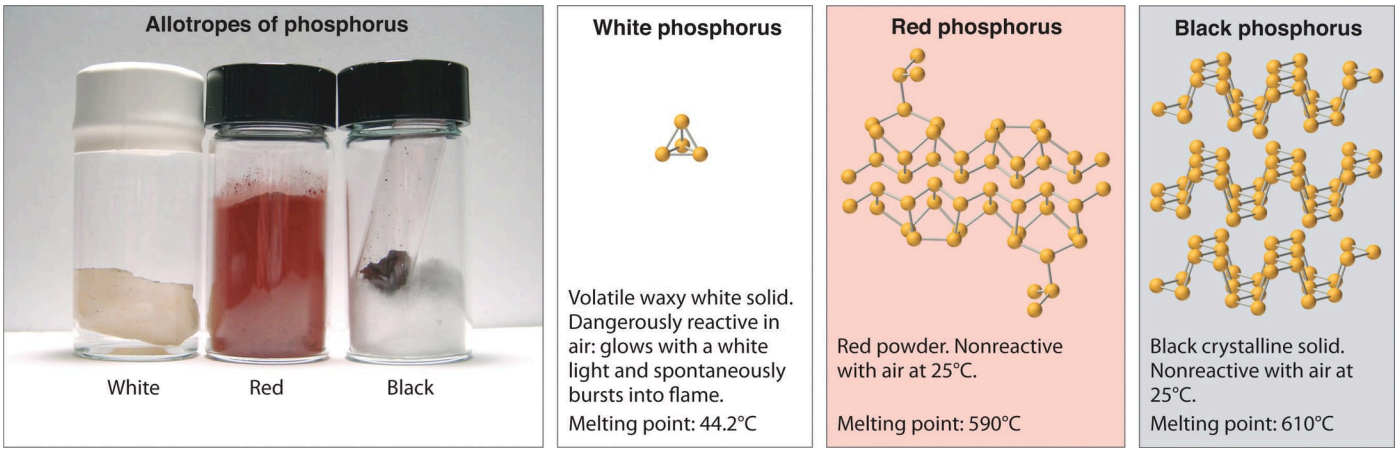


Figure 10.4.3*: The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus 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.

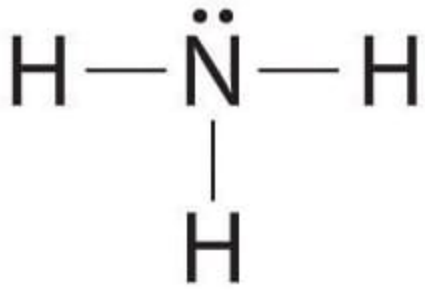
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- 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 8.5.2, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \tag{10.4.1}$$

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 8.5.2 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \tag{10.4.2}$$

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.

Note

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.

YouTube Video

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Lewis Structure of Charged Molecules: https://youtu.be/pTkziPtvMYU

Example 10.4.2

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

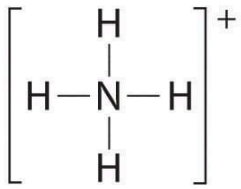
Asked for: formal charges

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 8.5.2 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



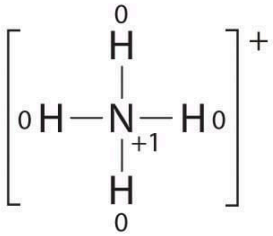
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation 8.5.1, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0 \tag{10.4.3}$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0 \tag{10.4.4}$$

The formal charges on the atoms in the NH_4^+ ion are thus

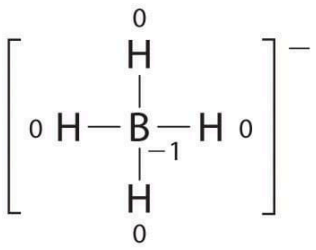


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 10.4.2

Write the formal charges on all atoms in BH_4^-.

Answer



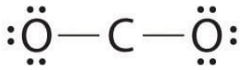
If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable Lewis Structures

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for CO_2. Both structures conform to the rules for Lewis electron structures.

CO_2

1. C is less electronegative than O, so it is the central atom.
2. C has 4 valence electrons and each O has 6 valence electrons, for a total of 16 valence electrons.
3. Placing one electron pair between the C and each O gives O–C–O, with 12 electrons left over.
4. Dividing the remaining electrons between the O atoms gives three lone pairs on each atom:



This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

5. No electrons are left for the central atom.
6. To give the carbon atom an octet of electrons, we can convert two of the lone pairs on the oxygen atoms to bonding electron pairs. There are, however, two ways to do this. We can either take one electron pair from each oxygen to form a symmetrical structure or take both electron pairs from a single oxygen atom to give an asymmetrical structure:



Both Lewis electron structures give all three atoms an octet. How do we decide between these two possibilities? The formal charges for the two Lewis electron structures of CO_2 are as follows:



Both Lewis structures have a net formal charge of zero, but the structure on the right has a +1 charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They

are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.

Note

The Lewis structure with the set of formal charges closest to zero is usually the most stable.

Example 10.4.3: The Thiocyanate Ion

The thiocyanate ion (SCN^-), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which is the preferred arrangement of electrons.

Given: chemical species

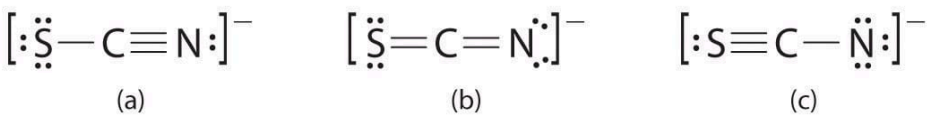
Asked for: Lewis electron structures, formal charges, and preferred arrangement

Strategy:

A. Use the step-by-step procedure to write two plausible Lewis electron structures for SCN^-.
B. Calculate the formal charge on each atom using Equation 8.5.1.
C. Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

Solution:

A Possible Lewis structures for the SCN^- ion are as follows:



(a) (b) (c)

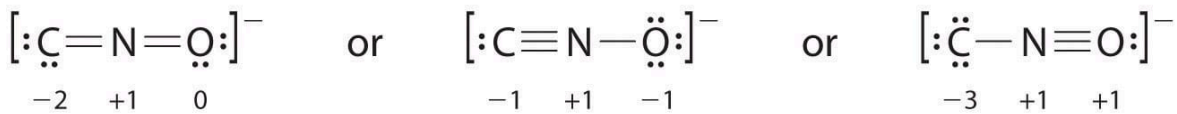
B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore $6-\left(6+\frac{2}{2}\right)=-1.5$ $-\left(4+\frac{4}{2}\right)=-1$ In (c), nitrogen has a formal charge of –2.

C Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, –1 versus +1, –2.

Exercise 10.4.3: The Fulminate Ion

Salts containing the fulminate ion (CNO^-) are used in explosive detonators. Draw three Lewis electron structures for CNO^- and use formal charges to predict which is more stable. (Note: N is the central atom.)

Answer



The second structure is predicted to be more stable.

Summary

- 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. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. If both electrons in a covalent bond come from the same atom, the bond is called a **coordinate covalent bond**. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families. Neutral compounds of group 14 elements typically contain four bonds around each atom (a double bond counts as two, a triple bond as three), whereas neutral compounds of group 15 elements typically contain three bonds. In cases where it is possible to write more than one Lewis electron structure with octets around all the nonhydrogen atoms of a compound, the **formal charge** on each atom in alternative structures must be considered to decide which of the valid structures can be excluded and which is the most reasonable. The formal charge is the difference between the number of valence electrons of the free atom and the number of electrons assigned to it in the compound, where bonding electrons are divided equally between the bonded atoms. The Lewis structure with the lowest formal charges on the atoms is almost always the most stable one.

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10.5: Resonance

Learning Objectives

- To understand the concept of resonance.

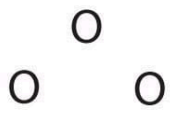
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding a single polyatomic species including fractional bonds and fractional charges. Resonance structure are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integer number of covalent bonds.

When 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°.

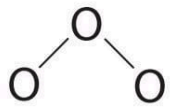
Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



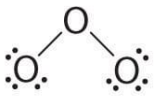
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



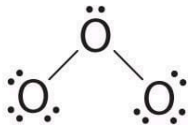
with 14 electrons left over.

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:

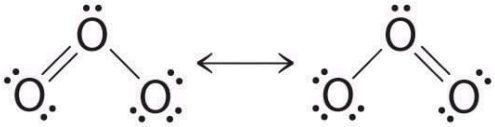


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



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.

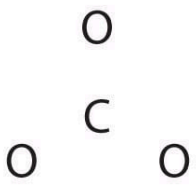
Note

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

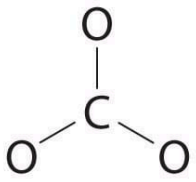
Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

1. Because carbon is the least electronegative element, we place it in the central position:

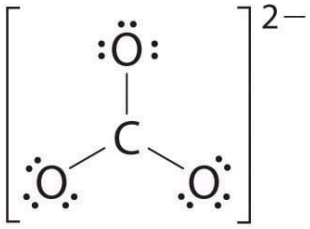


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the –2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

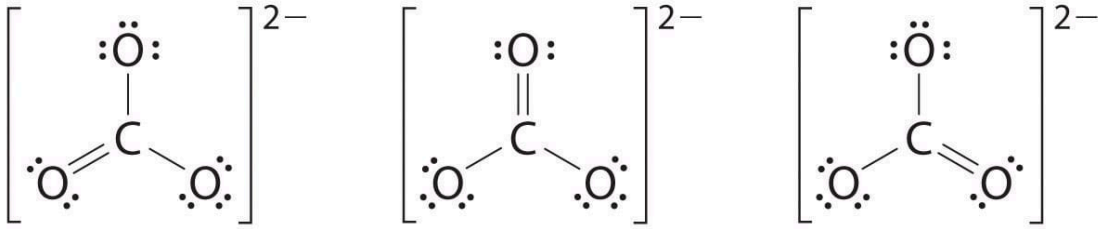


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the –2 charge:

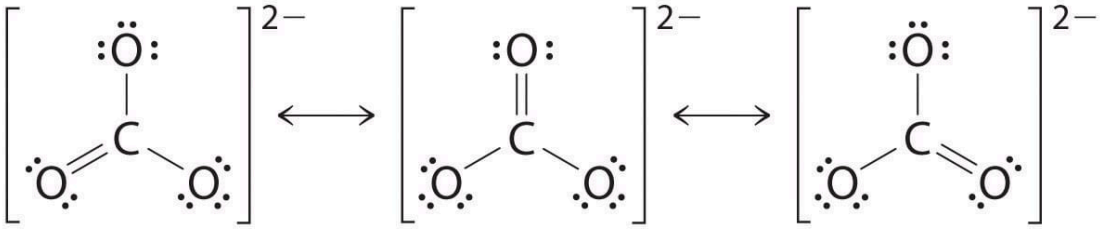


5. No electrons are left for the central atom.

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:

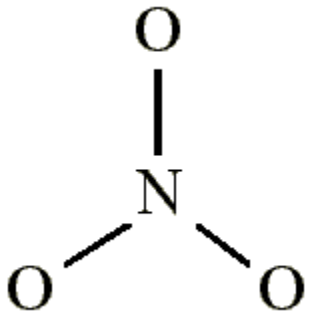


The actual structure is an average of these three resonance structures.

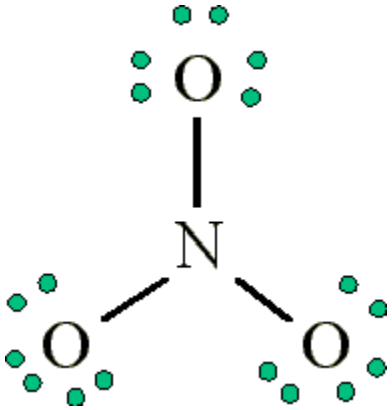
The Nitrate (NO_3^-) ion

1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

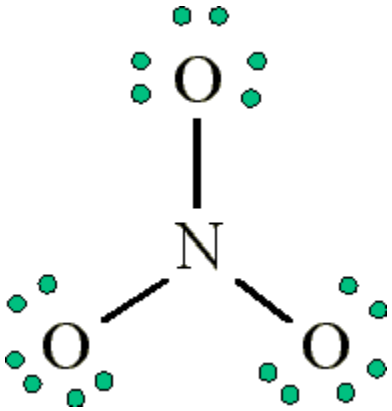
2. Draw the bond connectivities:



3. Add octet electrons to the atoms bonded to the center atom:

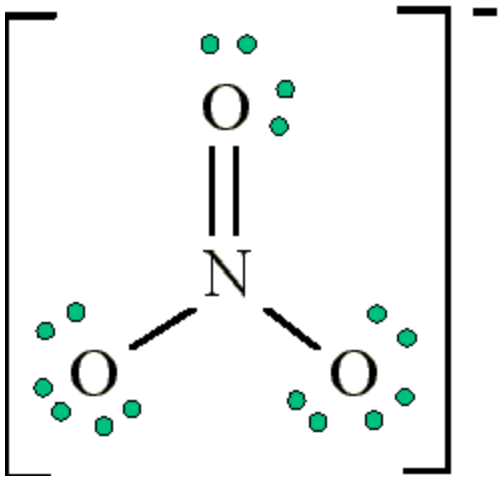


4. Place any leftover electrons (24-24 = **0**) on the center atom:



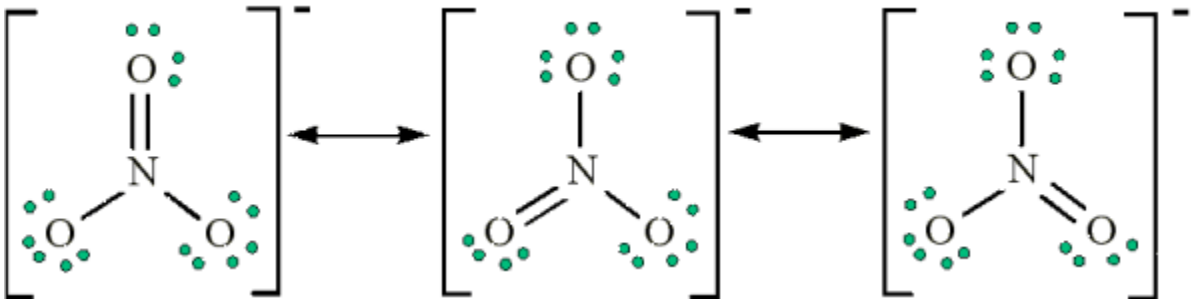
5. Does the central atom have an octet?

- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



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

Example 10.5.1: 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

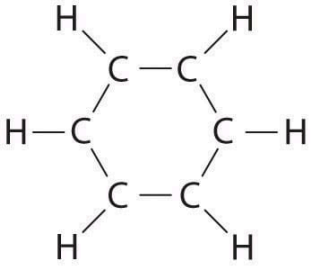
Asked for: resonance structures

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.

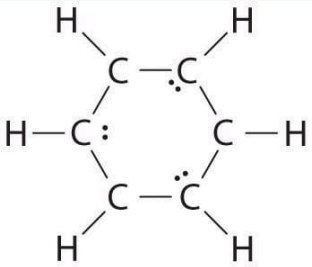
Solution:

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:



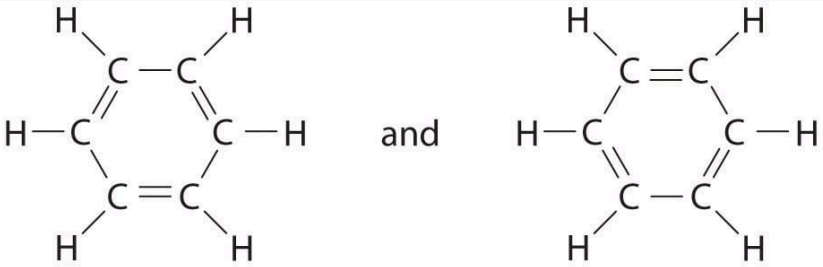
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

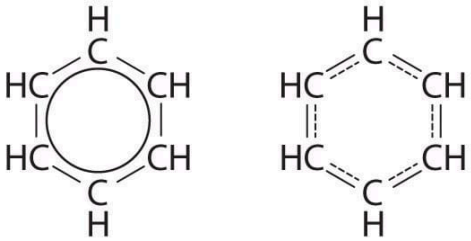


Three carbon atoms now have an octet configuration and a formal charge of –1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double 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:

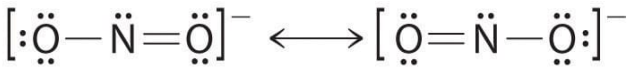


Benzene

Exercise 10.5.1: Nitrate Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



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.

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

Resonance Structures: https://youtu.be/aSP0D72MKe4

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.

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10.6: 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 (NO ,refer to figure one). 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 nitrogen monoxide. Nitrogen monoxide has 11 valence electrons. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitrogen monoxide had ten valence electrons we would come up with the Lewis Structure (Figure 10.6.1):

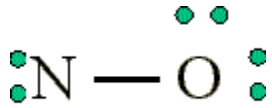


Figure 10.6.1: This is if Nitrogen monoxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure 10.6.2 based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure 10.6.1, 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 10.6.1, 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 nitrogen monoxide (Figure 10.6.2):

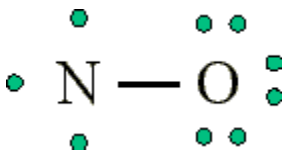


Figure 10.6.2: The proper Lewis structure for NO molecule

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, 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 was 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 $10.6.3$):

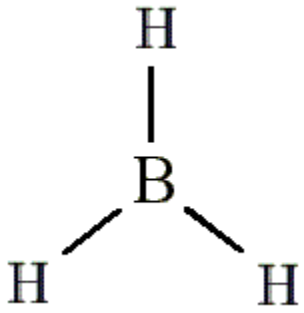


Figure $10.6.3$

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 $10.6.4$).



Figure $10.6.4$

If you look Figure $10.6.4$, 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 $10.6.5$):

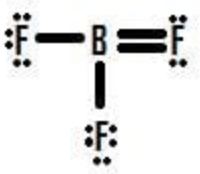


Figure 10.6.5

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 10.6.5, 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 10.6.6:

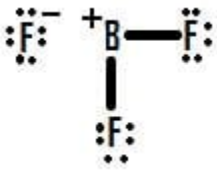


Figure 10.6.6

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 10.6.4), the one with the double bond (Figure 10.6.5), and the one with the ionic bond (Figure 10.6.6). The most contributing structure is probably the incomplete octet structure (due to Figure 10.6.5 being basically impossible and Figure 10.6.6 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 .

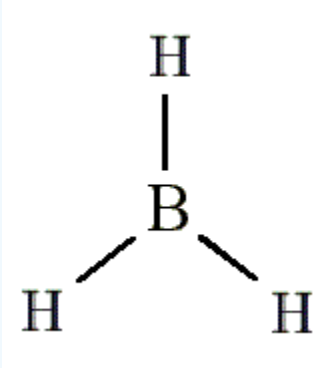
Example 10.6.1: NF_3

Draw the Lewis structure for boron trifluoride (BF_3).

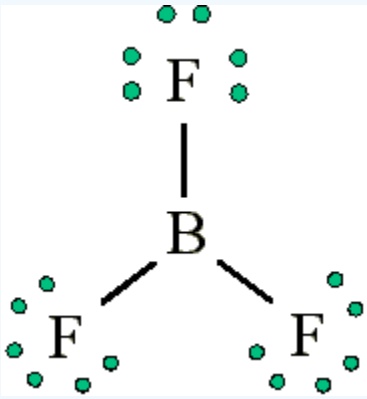
Solution

1. Add electrons (3*7) + 3 = **24**

2. Draw connectivities:



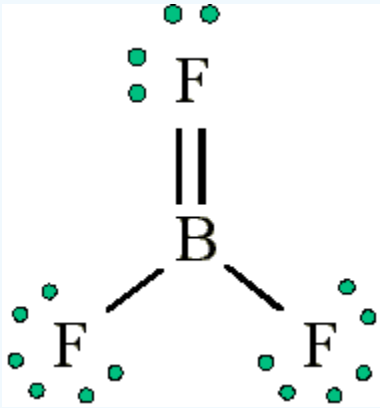
3. Add octets to outer atoms:



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:

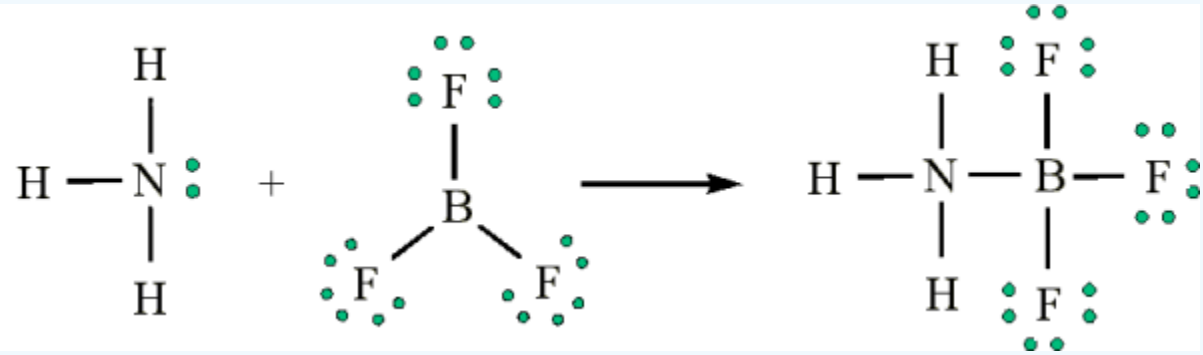


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

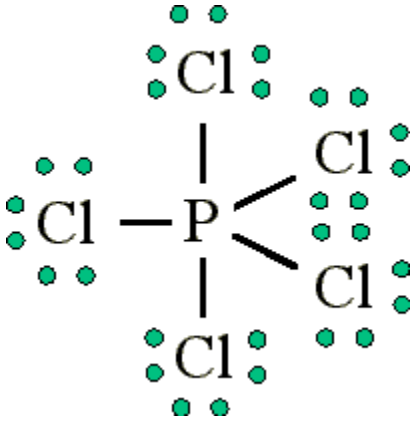
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single 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

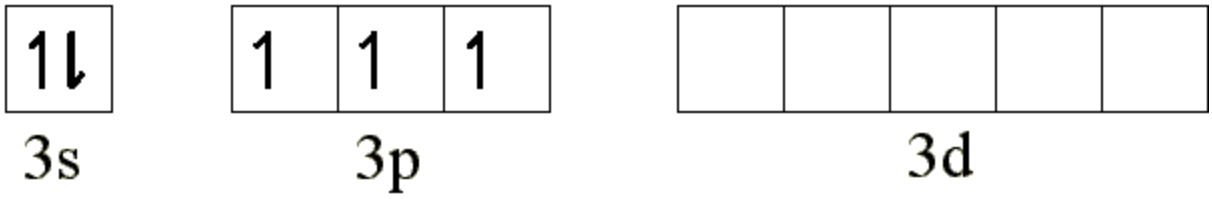
More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, 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:



Note

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.

Example 10.6.2: 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:

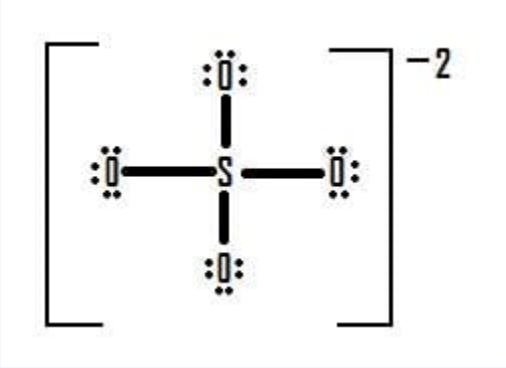


Figure 10.6.12

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:

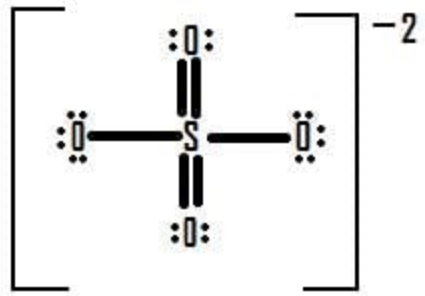


Figure 10.6.13

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 10.6.12, as opposed to +2 and -1 (difference of 3) in Figure 10.6.12) 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.

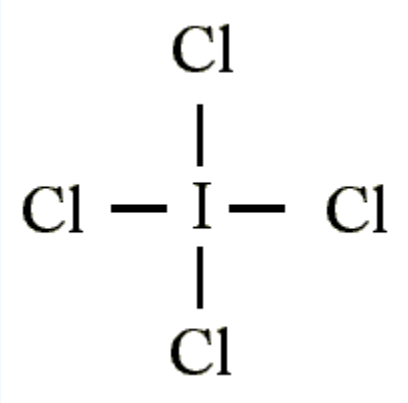
Example 10.6.3: The ICl_4^- Ion

Draw the Lewis structure for ICl_4^- ion.

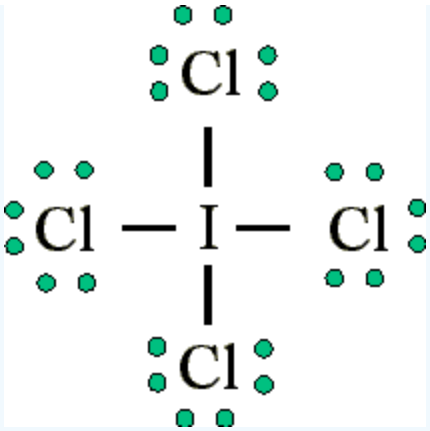
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

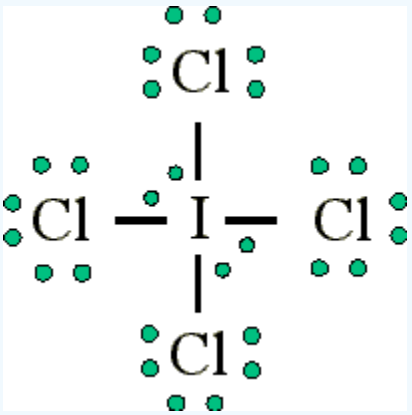
2. Draw the connectivities:



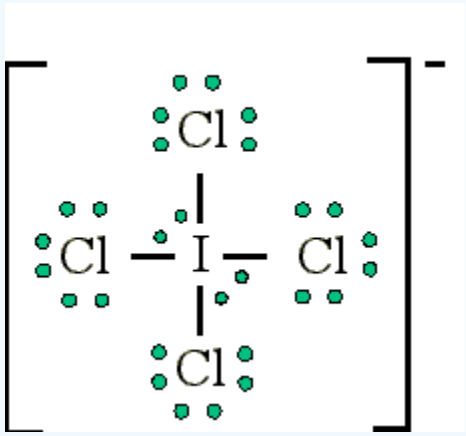
3. Add octet of electrons to outer atoms:



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.

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

Expanded Valence Shell Bonding: https://youtu.be/Y4fBdOJBSHI

Outside links

- http://www.saskschools.ca/curr_content/chem20/covmolec/exceptns.html
- student.ccbcmd.edu/~cyau1/121...ctetSp2006.pdf
- http://www.youtube.com/watch?v=KEQw9uQ8fUU
- www.rice.edu/~jenky/sports/antiox.html

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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10.7: Shapes of Molecules

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.

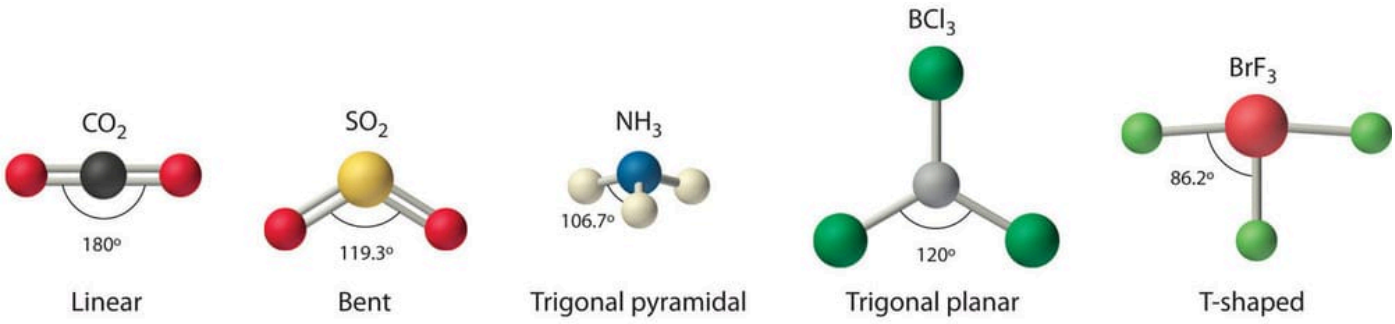


Figure 10.7.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

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 10.7.1 and 10.7.2.

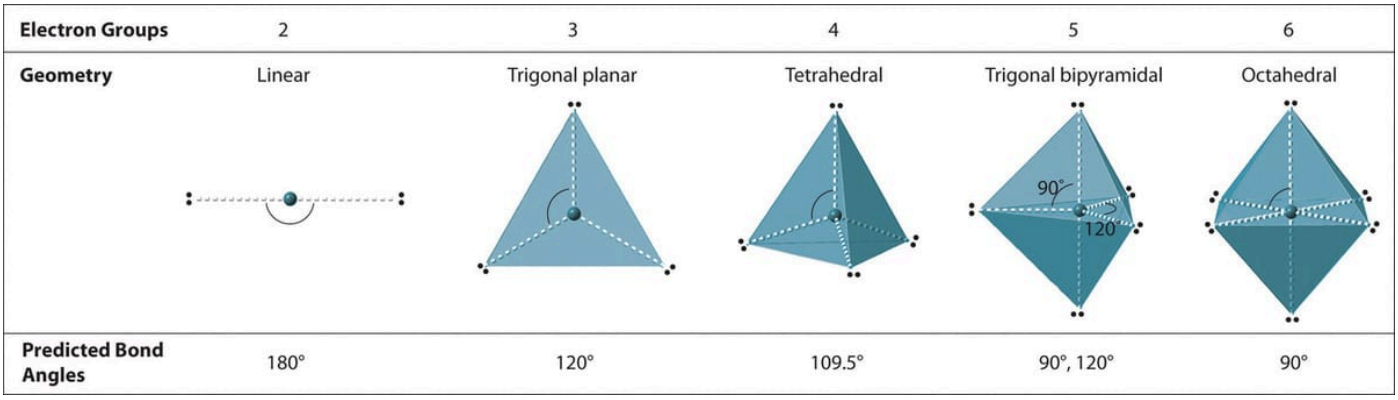


Figure 10.7.2: Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions. (CC BY-NC-SA; anonymous)

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 10.7.2 and Figure 10.7.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

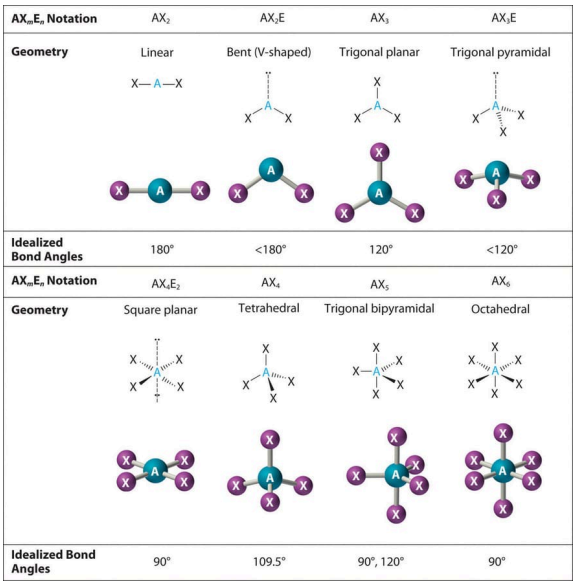


Figure 10.7.3: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line. (CC BY-NC-SA; anonymous)

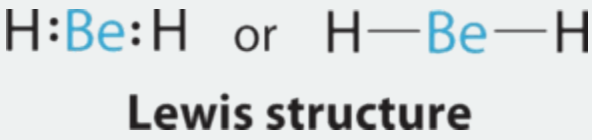
Linear, bent, trigonal planar, trigonal pyramidal, square planar, tetrahedral, trigonal bipyramidal, octahedral.

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



Lewis structure

Figure 10.7.2 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 10.7.3 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.

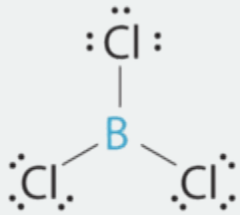
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

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 10.7.3). The structure of CO_2 is shown in Figure 10.7.1.

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

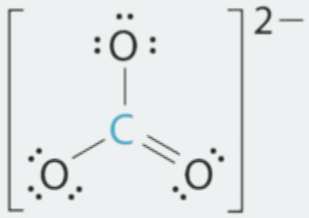
Figure 10.7.2): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 10.7.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 10.7.2.

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



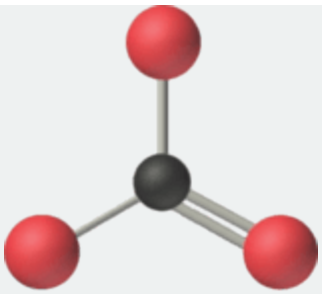
Lewis structure

Figure 10.7.2).

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 10.7.3 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.

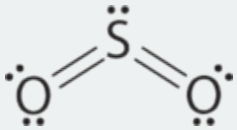


Figure 10.7.2): (CC BY-NC-SA; anonymous)

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 10.7.4). 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 10.7.2 and 10.7.3). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

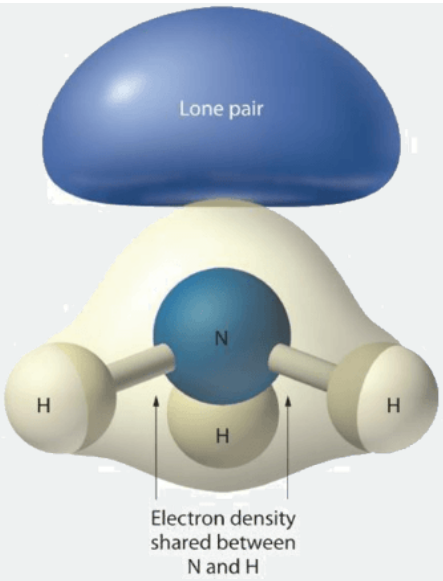
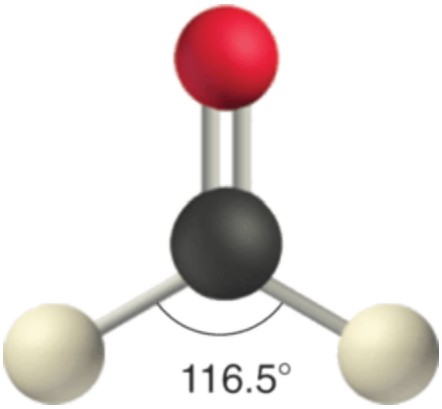


Figure 10.7.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair. (CC BY-NC-SA; anonymous)

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°).

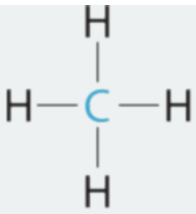


Four Electron Groups

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

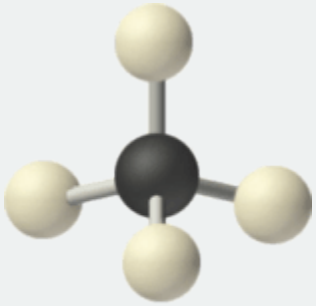


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 10.7.2, 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.

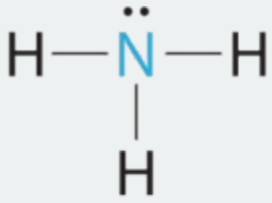
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 10.7.3).



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 10.7.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 10.7.3 and Figure 10.7.4).

AX_2E_2 Molecules: H_2O

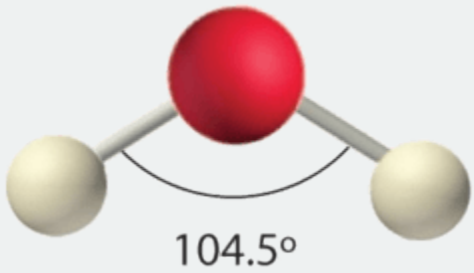
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



Figure 10.7.2: (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

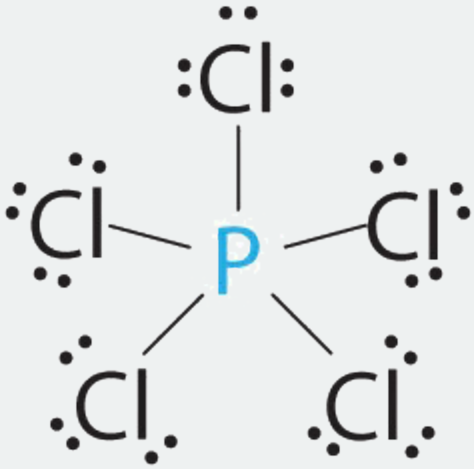
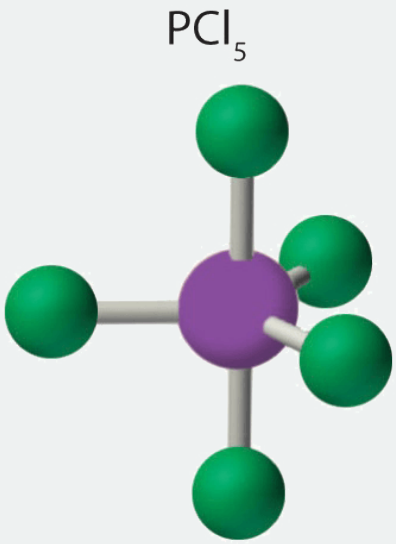


Figure 10.7.2): (CC BY-NC-SA; anonymous)

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 10.7.3. 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 10.7.2.

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.

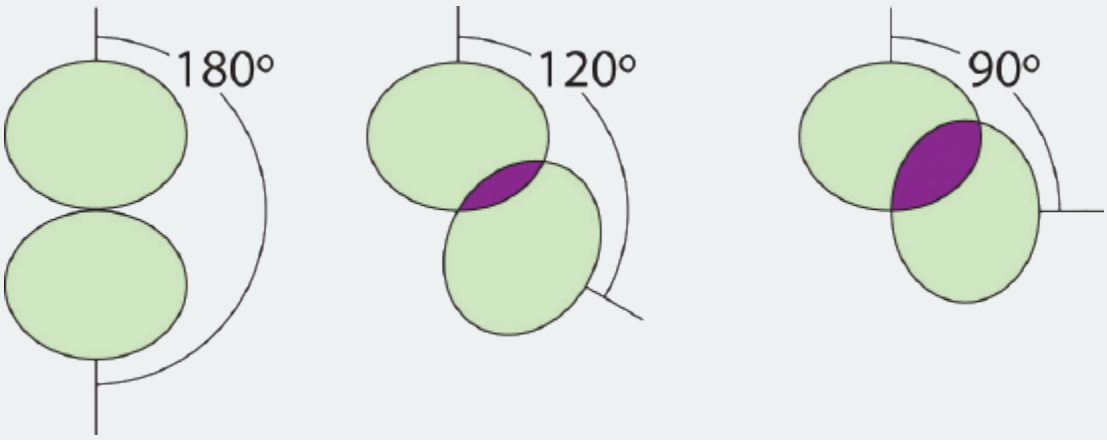
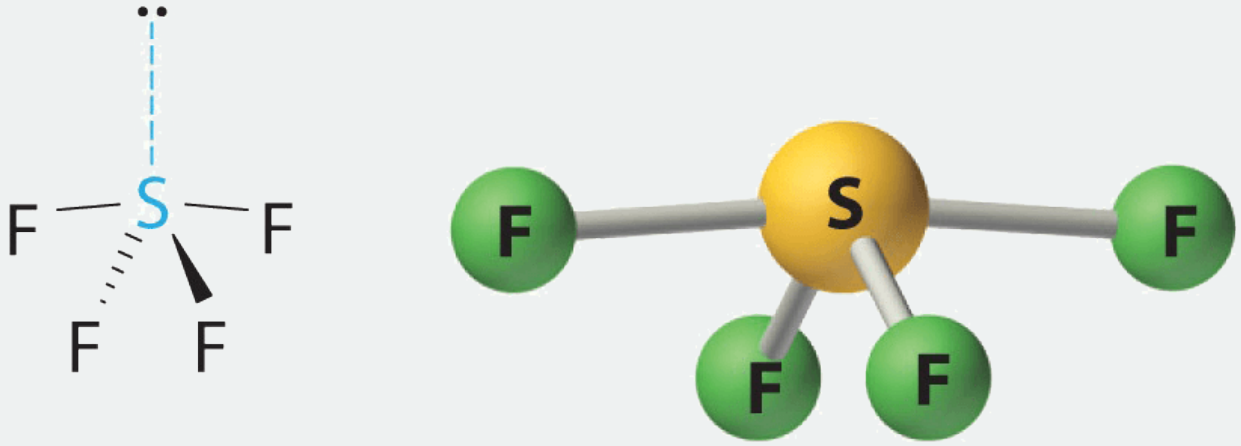


Figure 10.7.5: Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

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.

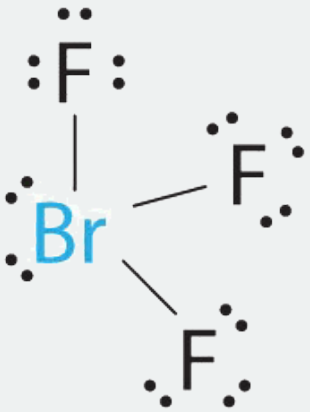
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



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



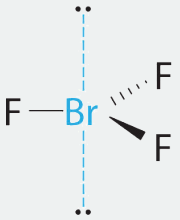
Lewis structure

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.

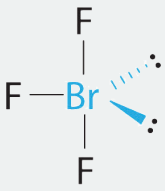
2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

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°:



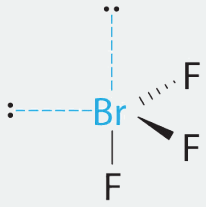
Lone pairs axial

(a)



Lone pairs equatorial

(b)



Lone pairs axial and equatorial

(c)

Interactions

90º LP–LP	0	0	1
90º 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 10.7.2.1).

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.

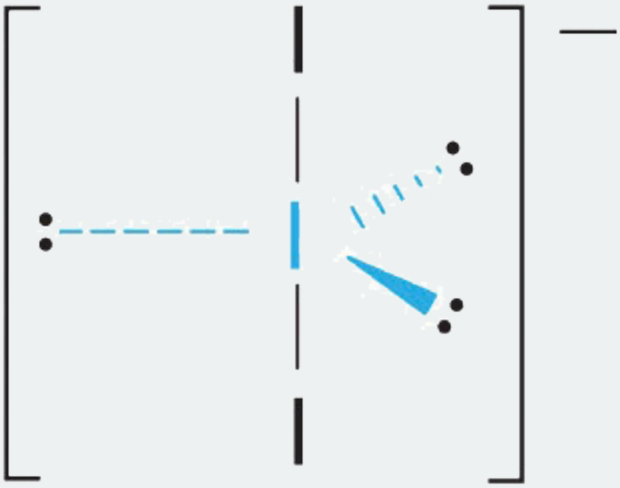
AX_2E_3 Molecules: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



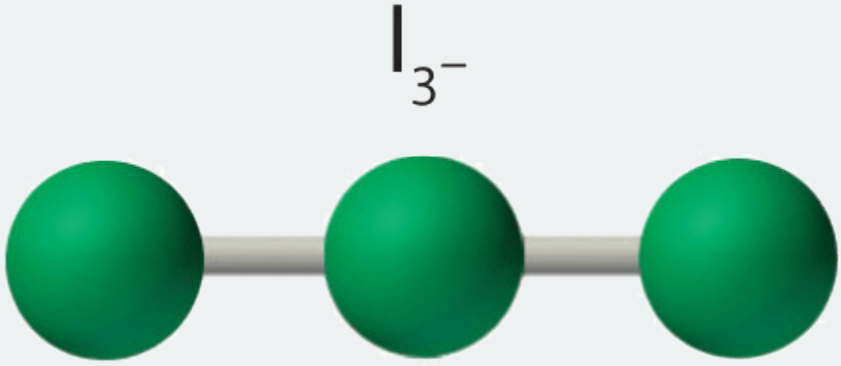
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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.

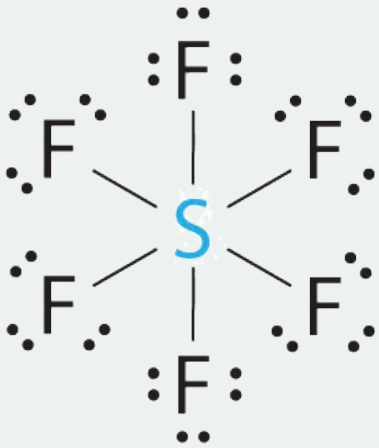


Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 10.7.2.)

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



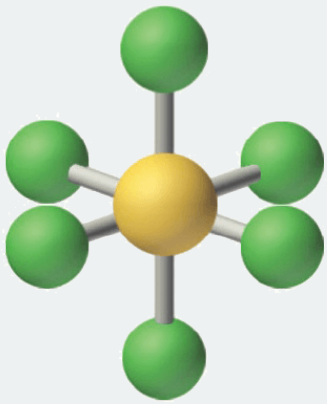
Lewis structure

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 $10.7.2$ 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.

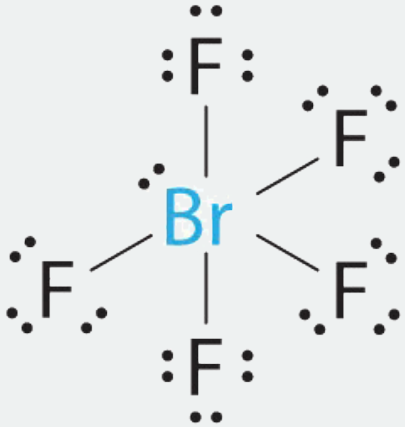
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



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

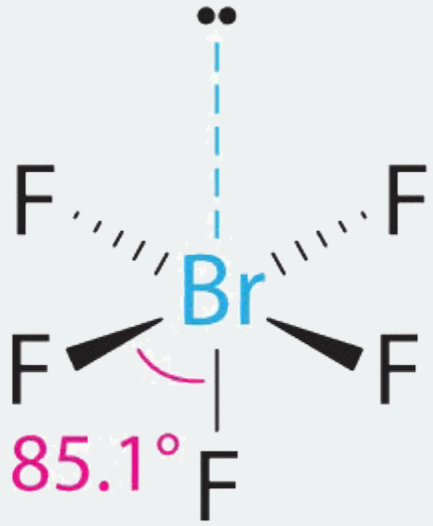


Lewis structure

Five fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has one lone pair.

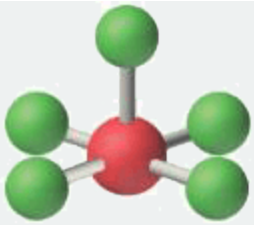
With its expanded valence, this species is an exception to the octet rule.

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.

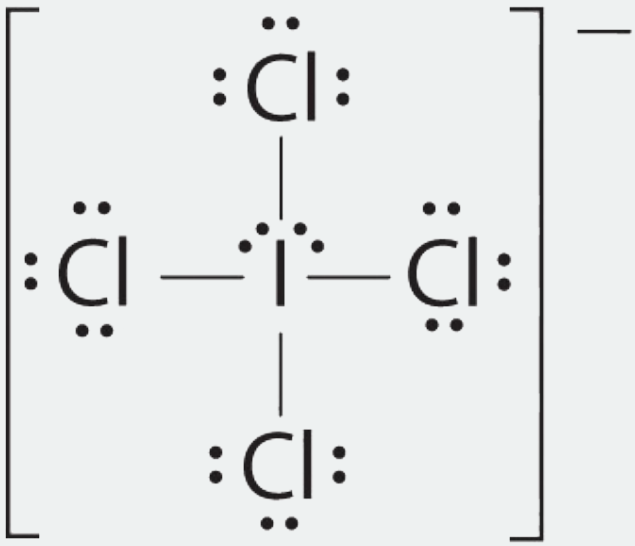
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is s*quare pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



Molecular geometry
(square pyramidal)

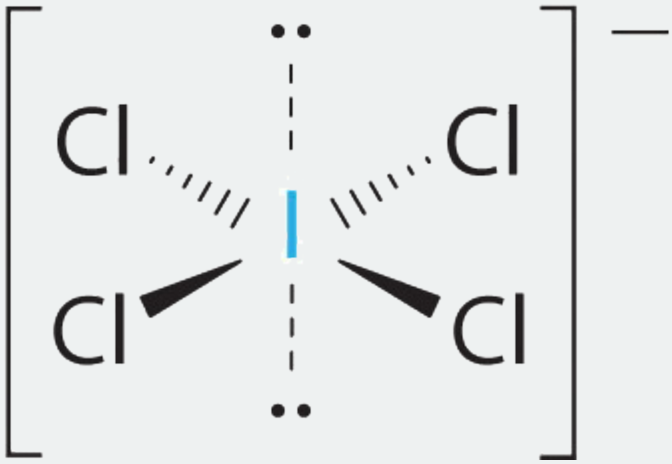
AX_4E_2 Molecules: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



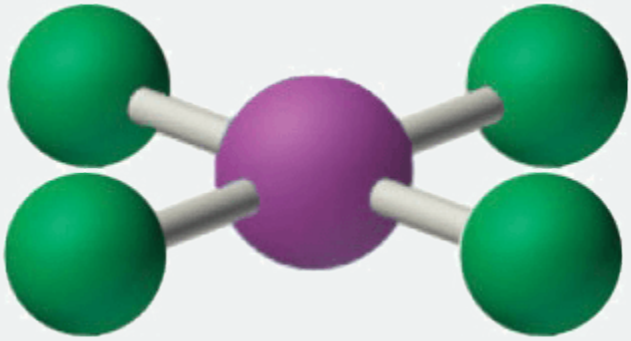
Four chlorines are bonded to a central iodine. Each chlorine has three electron pairs. The iodine has two electron pairs. The molecule is negatively charged.

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 10.7.6.

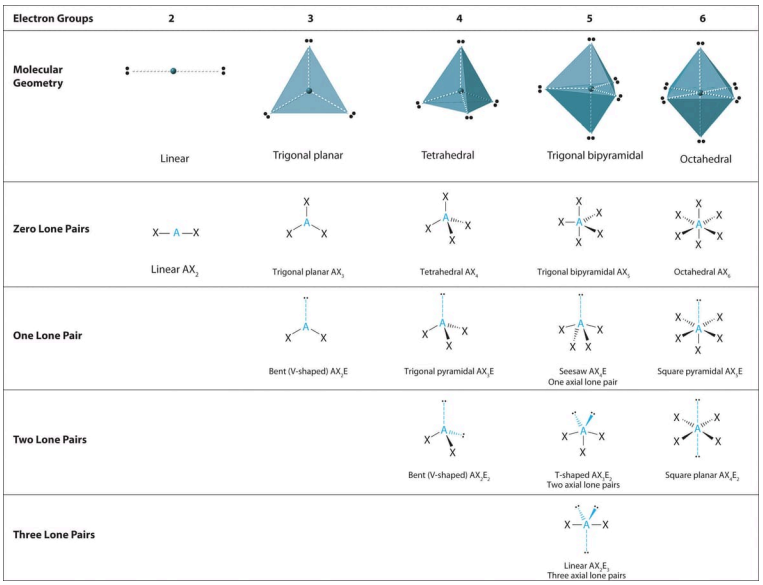


Figure 10.7.6***:*** *Overview of Molecular Geometries*

YouTube Video

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Example 10.7.1

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

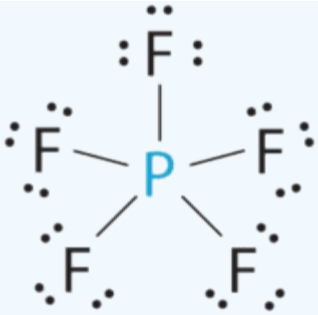


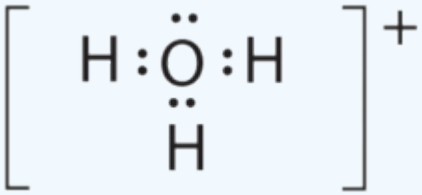
Figure 10.7.6): (CC BY-NC-SA; anonymous)

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

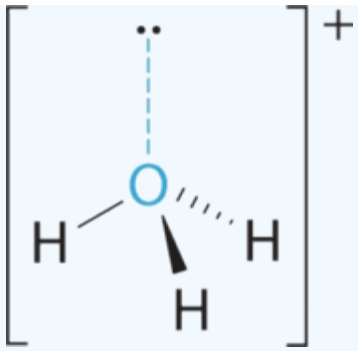


Three hydrogens are bonded to a central oxygen. The oxygen has two lone pairs. The molecule has a charge of plus one.

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 10.7.1

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 10.7.2

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 Example10.7.1.

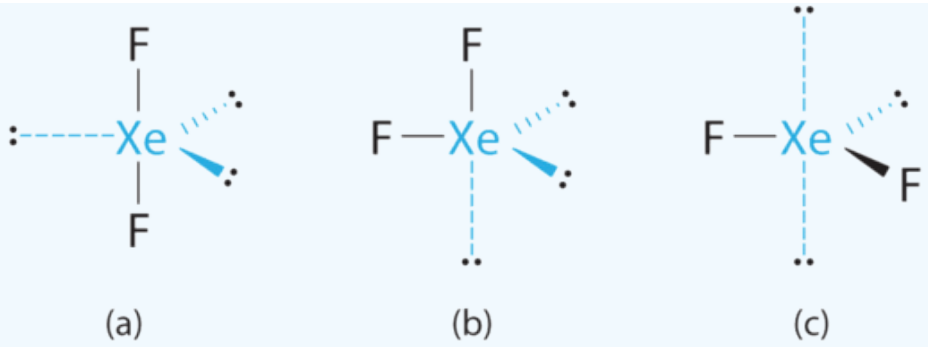
Solution:

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:



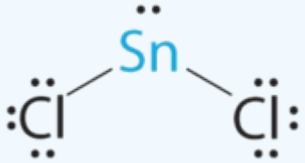
Interactions			
90 LP–LP	0	2	2

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 10.7.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a available at the end of this section.

YouTube Video

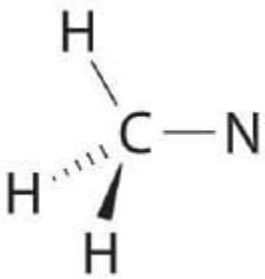
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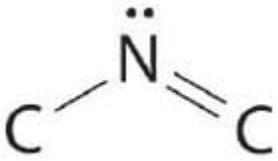
Molecules with No Single Central Atom

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:

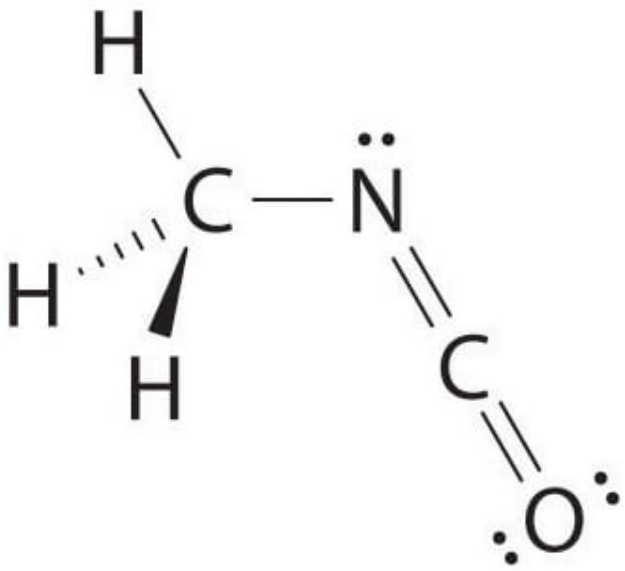


Figure 10.7.7).

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.

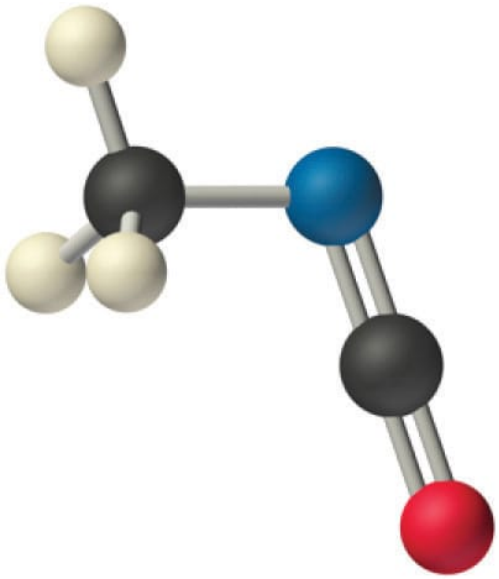


Figure 10.7.7: The Experimentally Determined Structure of Methyl Isocyanate

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 10.7.3

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 10.7.3 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 10.7.3

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 10.7.8*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 10.7.8*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.

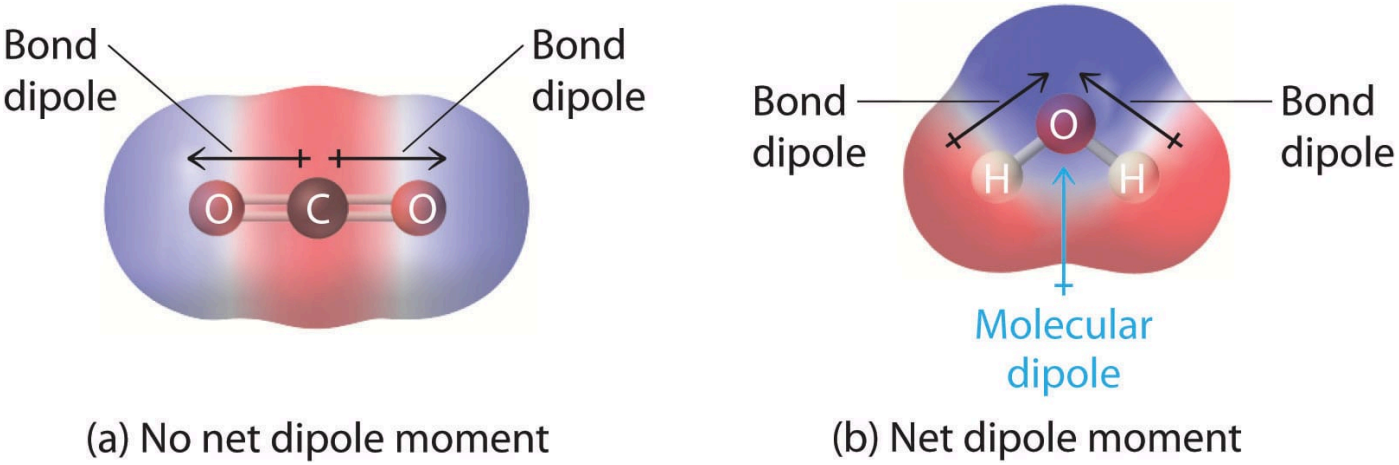


Figure 10.7.8: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 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 10.7.9. 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.

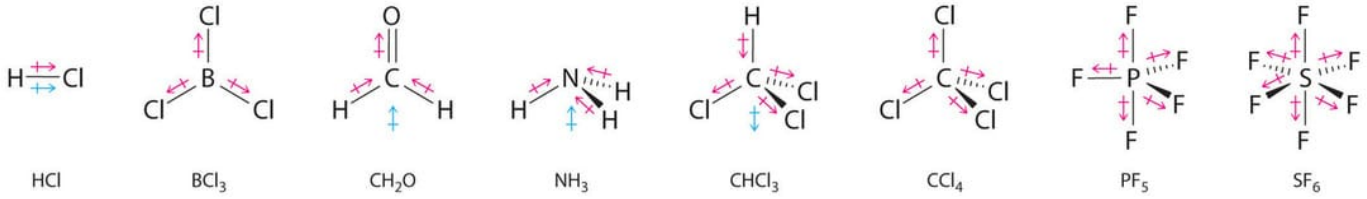


Figure 10.7.9: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

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Example 10.7.4

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

Given: three chemical compounds

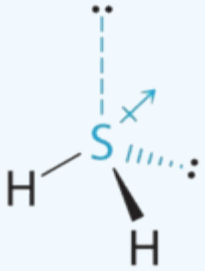
Asked for: net dipole moment

Strategy:

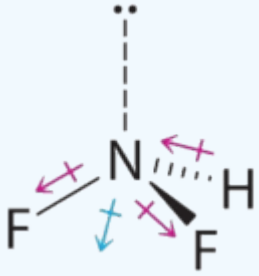
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

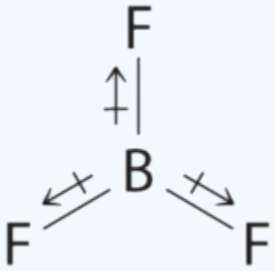
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 10.7.6). The bond dipoles cannot cancel one another, so the molecule has a net 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 10.7.4

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 10.7.1

trigonal pyramidal
octahedral
linear

Exercise 10.7.2

trigonal planar
square planar

Exercise 10.7.3

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

Exercise 10.7.4

CH_3Cl and XeO_3

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10.9: Bond Energies

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 10.9.1 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table 10.9.1: 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.

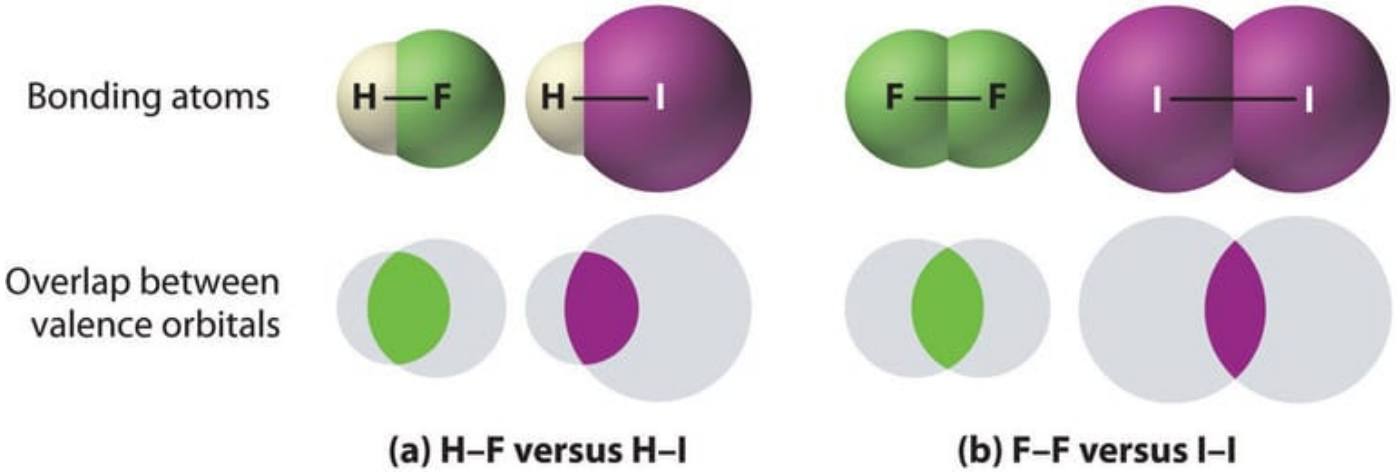


Figure 10.9.1: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) 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 10.9.2); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 10.9.1 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 10.9.2: 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 ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \tag{10.9.1}$$

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:

$$\mathrm{CH_3(CH_2)_5CH_3\,(l) + 11\,O_2\,(g) \;\rightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g)} \tag{10.9.2}$$

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)

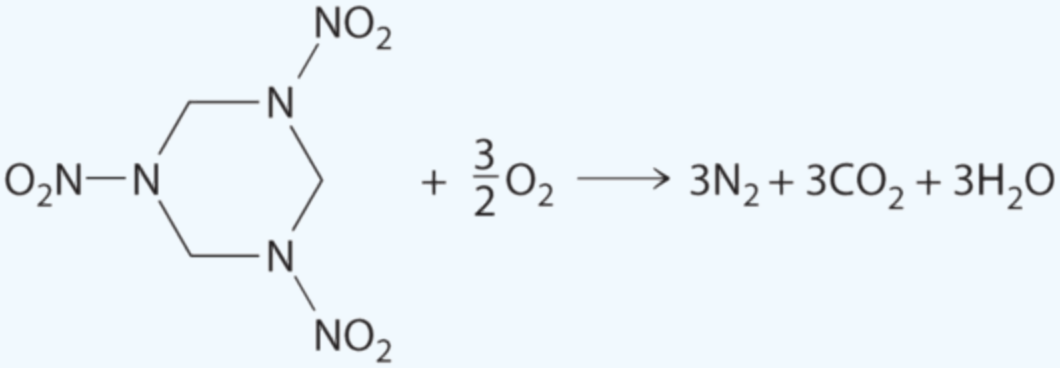
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

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 ($\Delta H_{rxn} = -4817\ kJ/mol$), 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 10.9.1: 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 10.9.1 to estimate the ΔH_{rxn} per mole of RDX.



RDX

Given: chemical reaction, structure of reactant, and Table $10.9.1$.

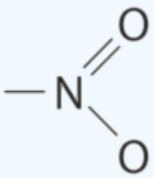
Asked for: ΔH_{rxn} per mole

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 $10.9.1$ 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 $10.9.1$, 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 10.9.1: 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:

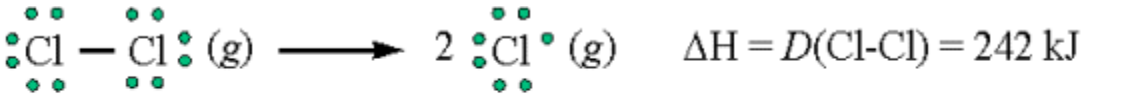
1,1-difluoroethylene reacts with <span class=HCL to produce CH3Cf2Cl and HCFC142b." data-cke-saved-src="/@api/deki/files/129585/imageedit_31_2777381278.png" src="/@api/deki/files/129585/imageedit_31_2777381278.png" data-quail-id="371">

Use tabulated bond energies to calculate ΔH_{rxn}.

Answer available at the end of this section.

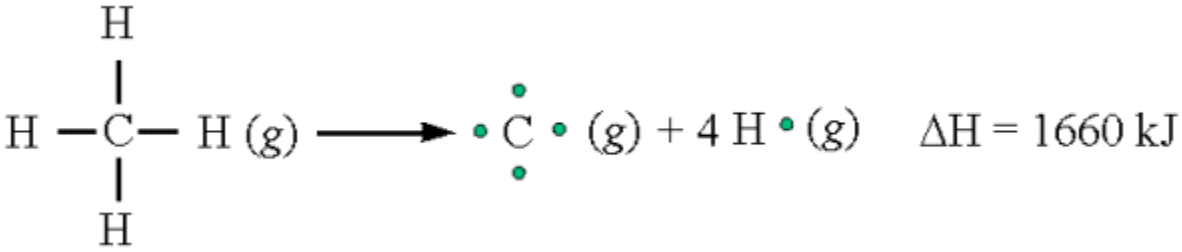
Bond Dissociation Energy

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 10.9.4: 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.

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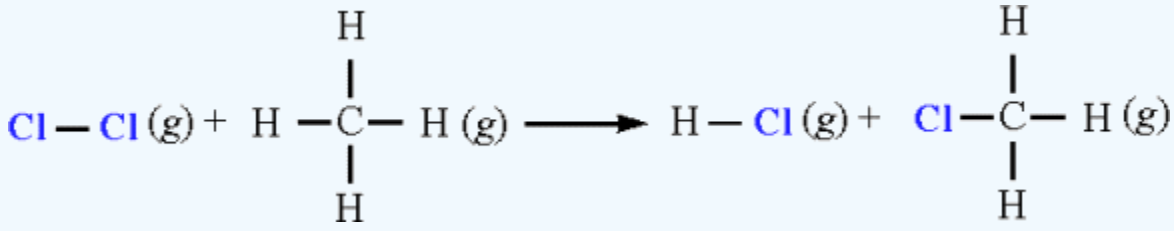
Bond Energies and the Enthalpy of Reactions

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:

$$\Delta H = \sum \text{bond energies of broken bonds} - \sum \text{bond energies of formed bonds} \tag{10.9.3}$$

Example 10.9.2: Chlorination of Methane

What is the enthalpy of reaction between 1 mol of chlorine and 1 mol methane?



Solution

We use Equation 10.9.3, 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

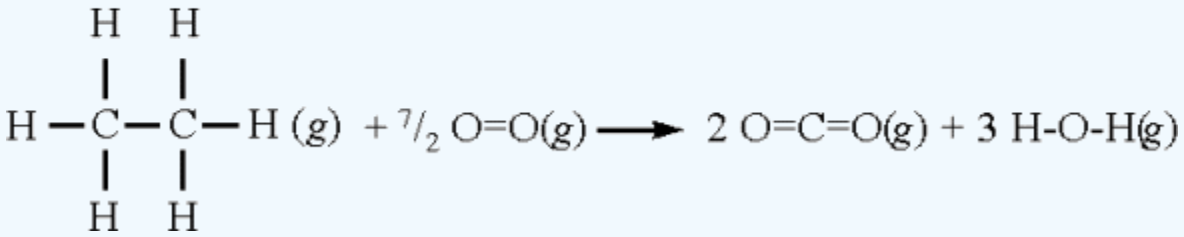
$$\begin{aligned}\Delta H &= [D(Cl-Cl)+D(C-H)]-[D(H-Cl)+D(C-Cl)]\\ &= [242kJ+413kJ]-[431kJ+328kJ]\\ &= -104\,kJ\end{aligned}$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

Example 10.9.3: 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 10.9.3, 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 10.9.5: 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.

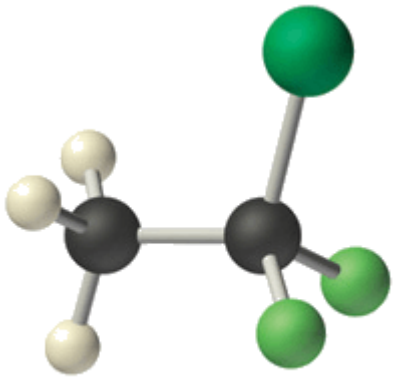
The breakage and formation of bonds is similar to a relationship: you can either get married or divorced and it is more favorable to be married.

- 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 10.9.1**: Freon**

–54 kJ/mol



HCFC-142b

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- 8.8: Strength of Covalent Bonds is licensed CC BY-NC-SA 3.0.

11: CHEMICAL BONDING II: ADDITIONAL ASPECTS

Petrucci: ***General Chemistry***
Principles and Modern Applications

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11.1: What a Bonding Theory Should Do

As we have talked about using Lewis structures to depict the bonding in organic 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?

In this chapter, the **valence bond theory** is introduced to describe bonding in organic 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. In order to explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

Valence bond theory is adequate for describing many aspects of organic structure. In some cases, however, chemists need to use a different model, called **molecular orbital (MO) theory**, to talk about covalent bonds in which electrons are shared not just between two atoms, but between several, or even over an entire molecule.

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.

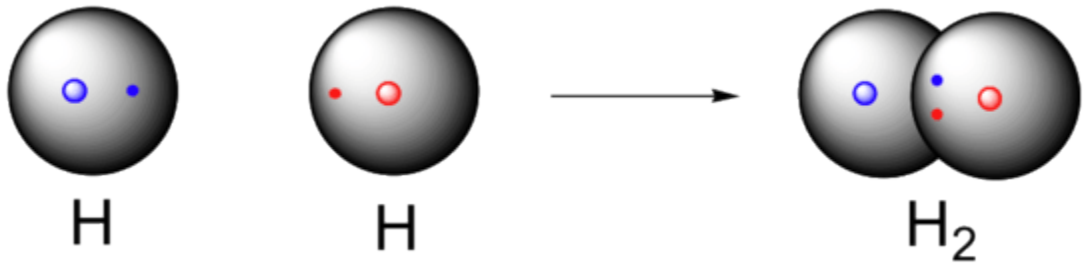


Figure 11.1.1: Addition of twe hydrogen atoms to form the diatomic hydrogen molecule.

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.

But 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.

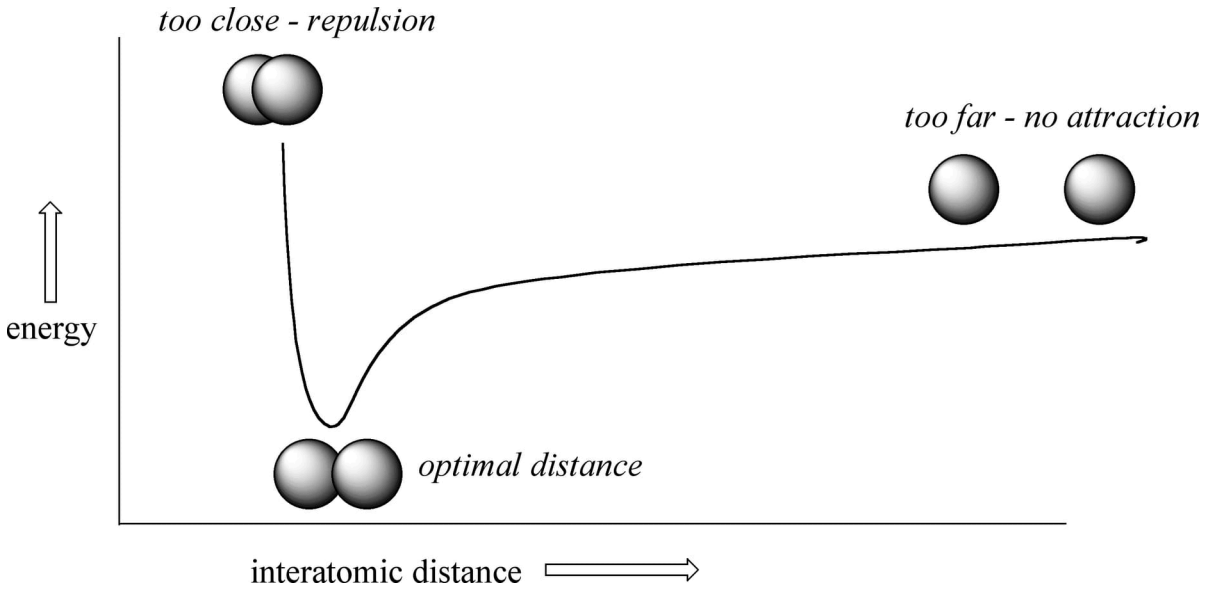


Figure 11.1.2.: Potential of interaction for the addition of twe hydrogen atoms to form the diatomic hydrogen molecule.

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.

It is not accurate, however, 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.

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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11.2: Introduction to the Valence-Bond Method

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.

Valence Bond Theory: A Localized Bonding Approach

Valence Bond Theory has its roots in Gilbert Newton Lewis's paper *The Atom and The Molecule*. Possibly unaware that Lewis's model existed, Walter Heitler and Fritz London came up with the idea that resonance and wavefunctions contributed to chemical bonds, in which they used dihydrogen as an example. Their theory was equivalent to Lewis's theory, with the difference of quantum mechanics being developed. Nonetheless, Heitler and London's theory proved to be successful, providing Linus Pauling and John C. Slater with an opportunity to assemble a general chemical theory containing all of these ideas. Valence Bond Theory was the result, which included the ideas of resonance, covalent-ionic superposition, atomic orbital overlap, and hybridization to describe chemical bonds.

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. 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 11.2.1).

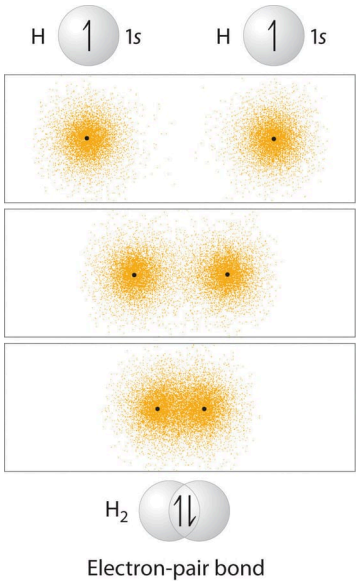


Figure 11.2.1: Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres 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 both 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 11.2.2 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 $n = 2$. Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

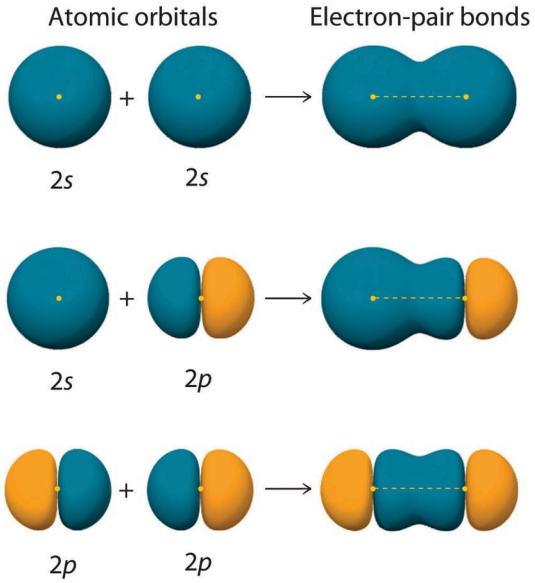


Figure 11.2.2: Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two *ns* atomic orbitals (a), an *ns* and an *np* atomic orbital (b), and two *np* atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Note

An important aspect of Valence Bond theory is the concept of maximum overlap to form the strongest possible covalent bonds.

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:



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 2s 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.

Reliability of Valence Bond Theory and Uses

As one can see, Valence Bond Theory can help describe how bonds are formed. However, there are some notable failures when it comes to Valence Bond Theory. One such failure is dioxygen. Valence Bond Theory fails to predict dioxygen's paramagnitism; it predicts that oxygen is diamagnetic. A species is paramagnetic if electrons are not spin paired and diamagnetic if the electrons are spin paired. Since Valence Bond theory begins with the basis that atomic orbitals overlap to create bonds and through that reasoning, one can see that electrons are spin paired when bonds overlap, dioxygen is indeed predicted to be diamagnetic if Valence Bond Theory is used. In reality, that is not the case. Also, sp^2d and sp^3 both have a coordinate number of four. Thus, Valence Bond Theory cannot predict whether the molecule is a square planar or the other shape (3). One must correctly draw the Lewis structure and use VSEPR to determine the shape.

Contributors and Attributions

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11.3: Hybridization of Atomic Orbitals

Learning Objectives

- To describe the hybridication in the bonding of simple compounds via valence bond theory.

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.

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 11.3.0.

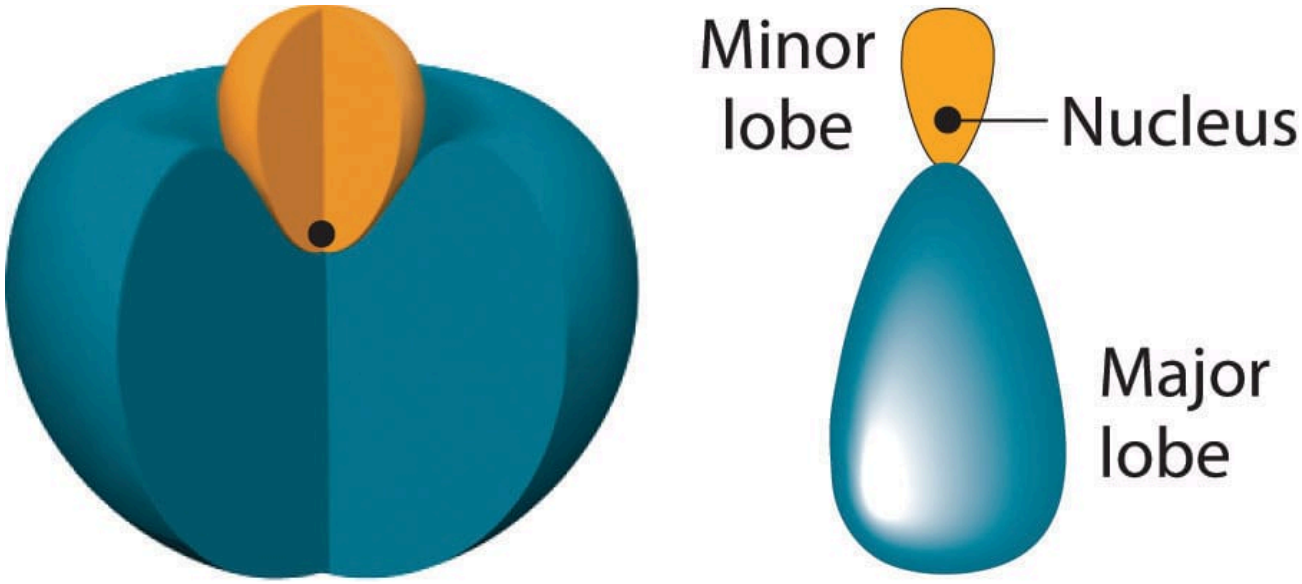


Figure 11.3.0: The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference A – B can also be written as A + (–B), in Figure 11.3.1 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 11.3.1, 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.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{11.3.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{11.3.2}$$

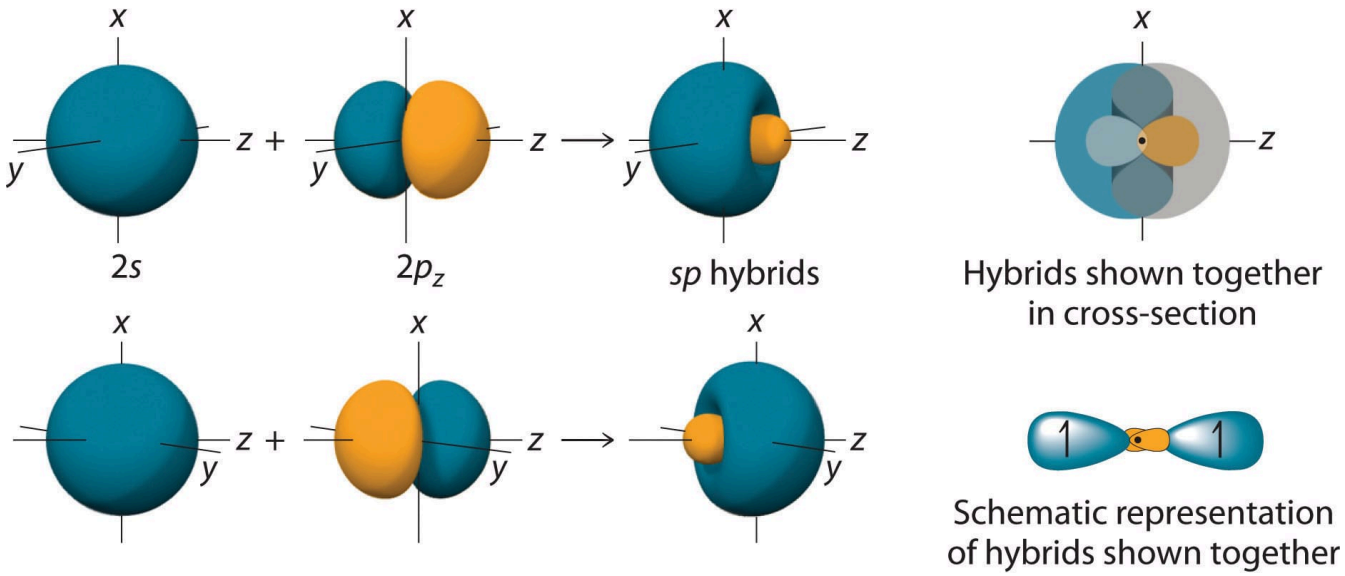


Figure 11.3.1: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

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:

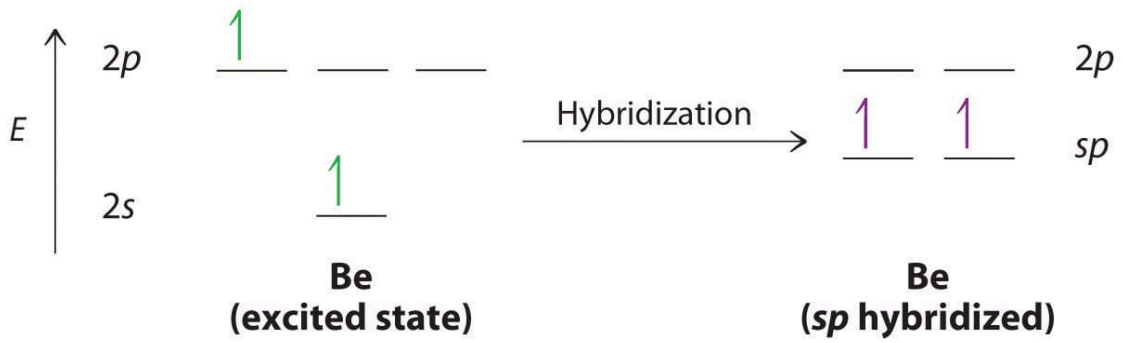


Figure 11.3.2, each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1s atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure 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.

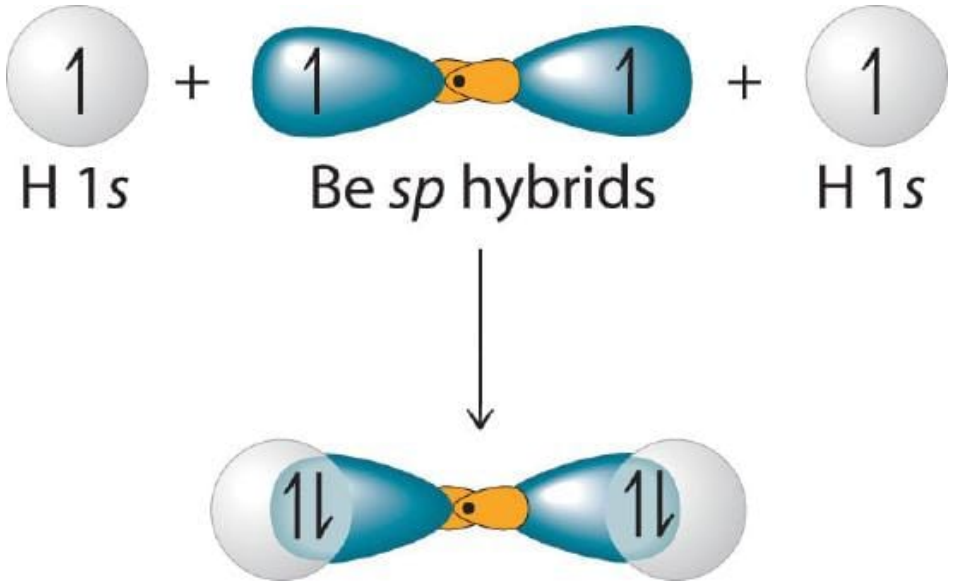


Figure 11.3.2: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1s orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule 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 11.3.3). 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.

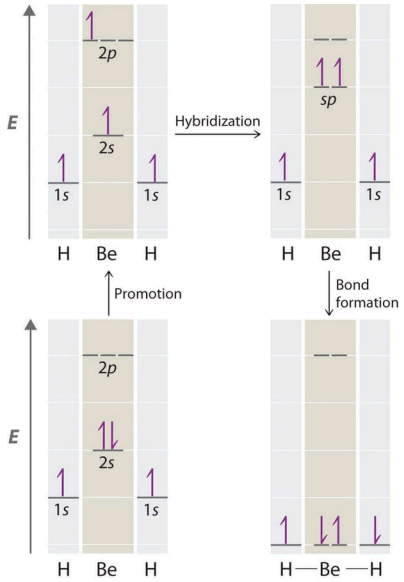


Figure 11.3.3: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom 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.

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:

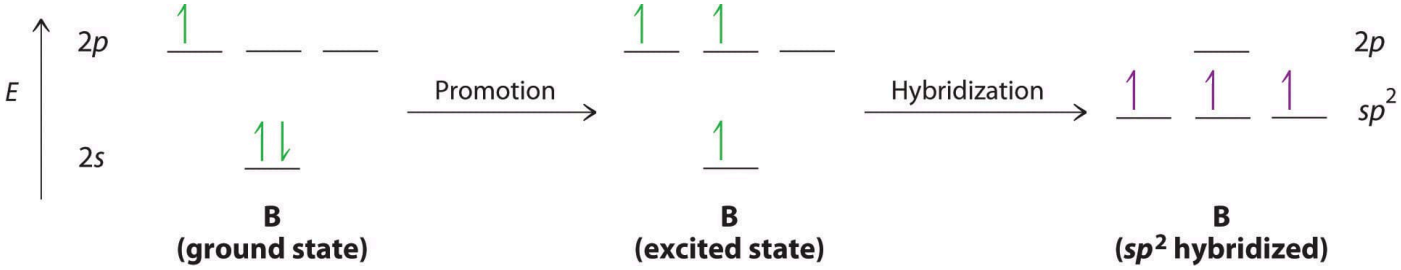


Figure 11.3.4). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

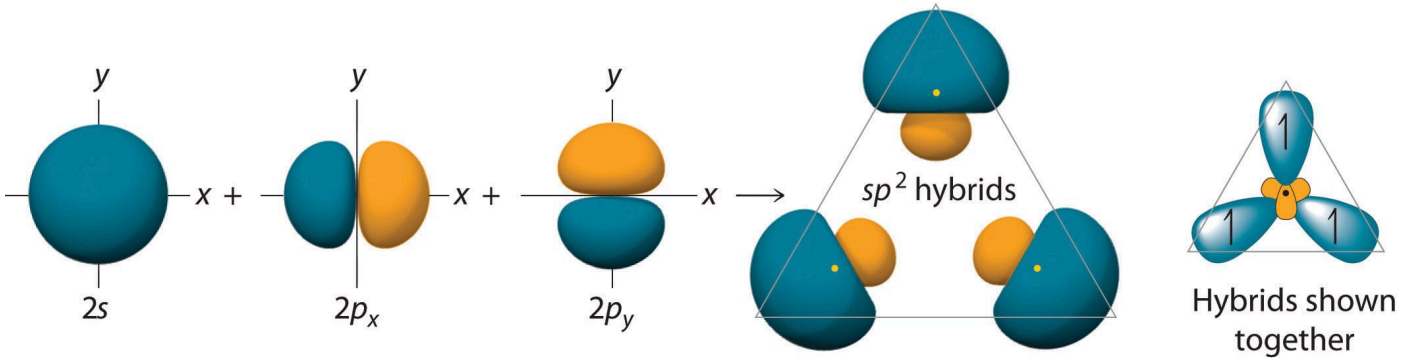
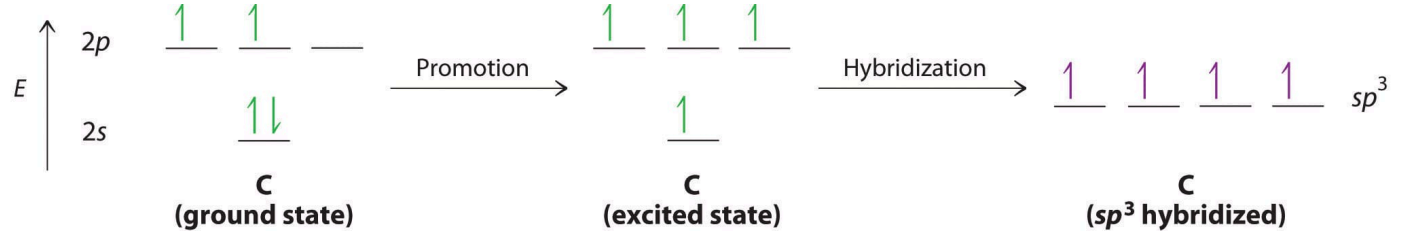


Figure 11.3.4: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

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:



The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 11.3.5). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

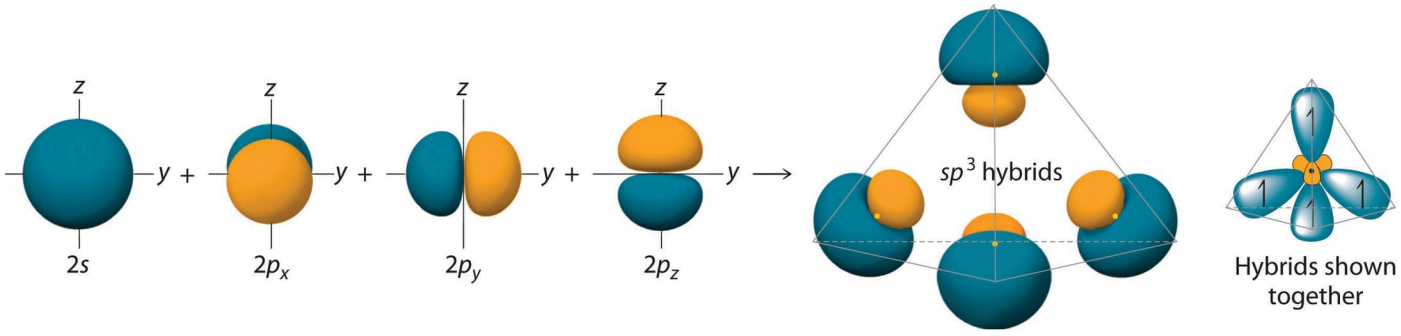


Figure 11.3.5: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

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 form in only 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 CH_4 and NH_3, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

YouTube Video

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View this YouTube Video online

Valence Bond Method & sp3 Hybridization: https://youtu.be/2hxKLGWQ5EQ

Example 11.3.1

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 VPSER 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 11.3.1

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. 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.
b. 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.

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 11.3.6). 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 11.3.6). 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.

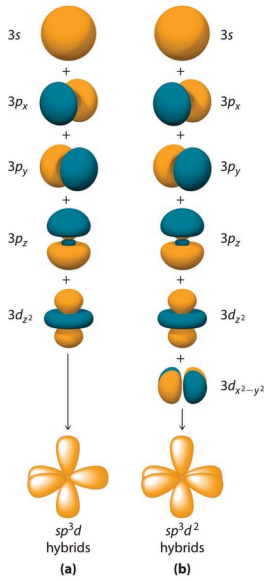


Figure 11.3.6: Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

Example 11.3.2

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

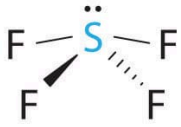
Asked for: hybridization of the central atom

Strategy:

A. Determine the geometry of the molecule using the strategy in Example 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 11.3.2

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. sp^3 with four P–Cl bonds
b. sp^3d with three Br–F bonds and two lone pairs
c. sp^3d^2 with six Si–F bonds

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 2s, 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.

Example 11.3.3: 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 2s 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 11.3.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer sp^3d^2 hybridization; no

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Expanded Octet Hybridization: https://youtu.be/1WpxXcKl_Io

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 $\boldsymbol{sp^2}$ **hybrids** or four equivalent $\boldsymbol{sp^3}$ **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 $\boldsymbol{sp^3d^2}$ **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.

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11.4: Multiple Covalent Bonds

Learning Objectives

- To explain resonance structures using molecular orbitals.

So far in our molecular 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.

Non-singular 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. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + s) and one C–C (sp^2 + sp^2) (part (a) in Figure 11.4.1). The sp^2 hybridization can be represented as follows:

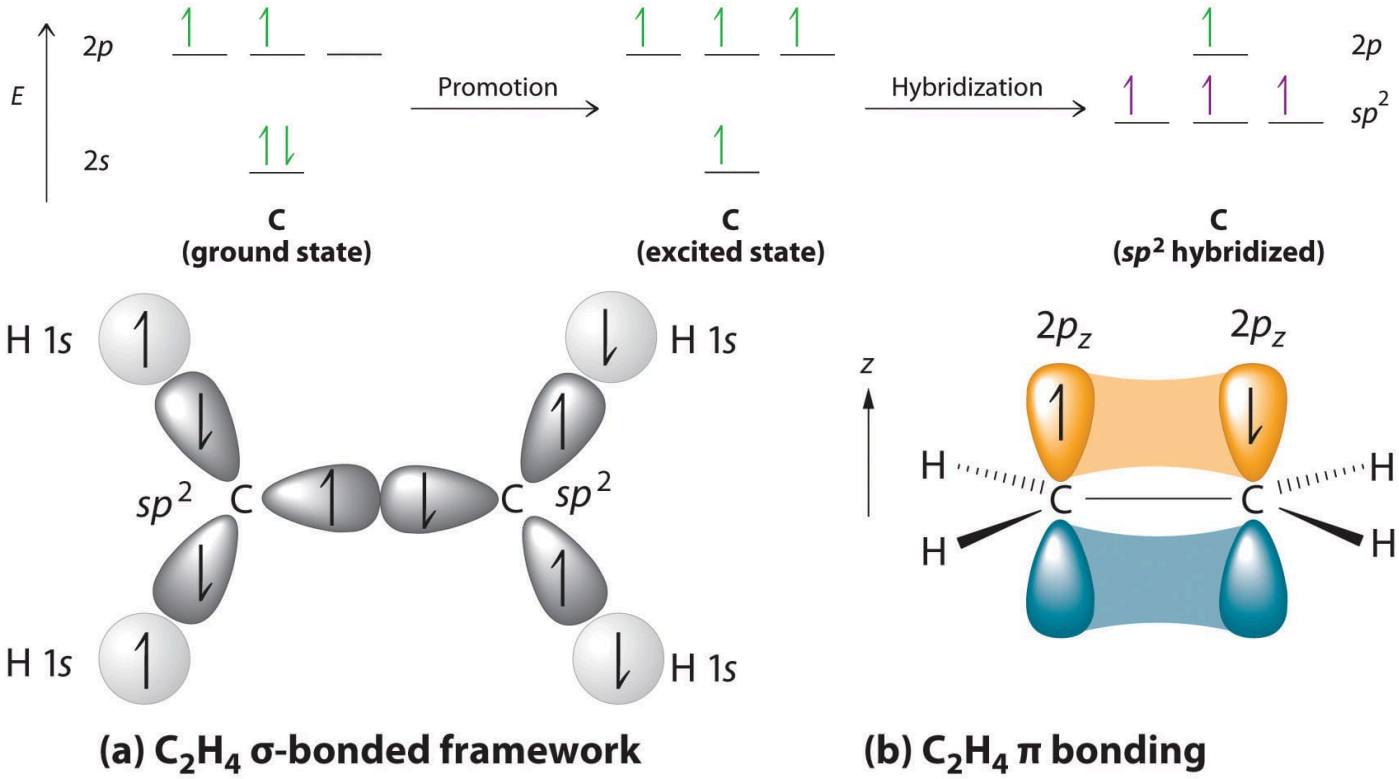


Figure 11.4.1: Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four 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.)

After hybridization, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure 11.4.1). The two singly occupied $2p_z$ orbitals can overlap to form a π bonding orbital and a π* antibonding orbital, which produces the energy-level diagram shown in Figure 11.4.2. With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. The π* orbital lies outside the internuclear region and has a

nodal plane perpendicular to the internuclear axis. 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.

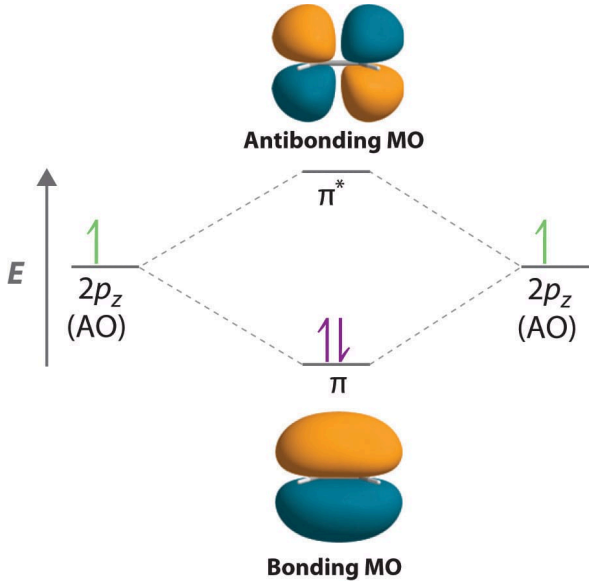


Figure 11.4.2: Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene. As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.

YouTube Video

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sp2 Hybridization: https://youtu.be/EepTvePnfBA

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 11.4.3).

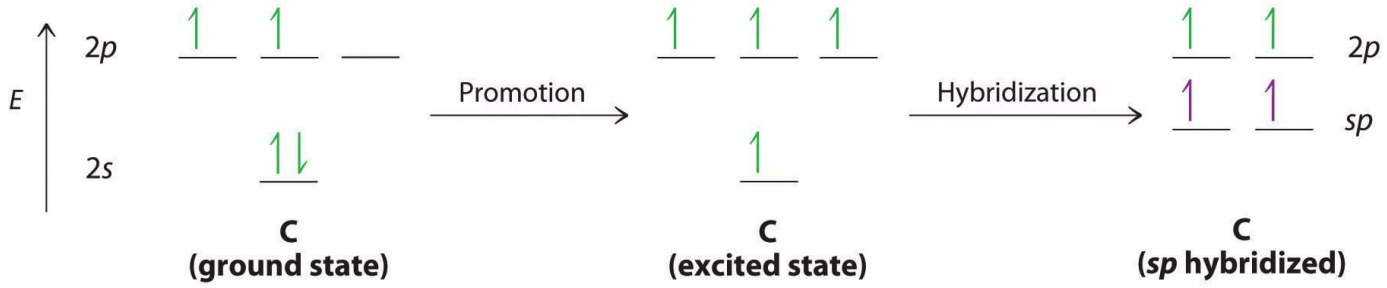


Figure 11.4.3). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular 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.

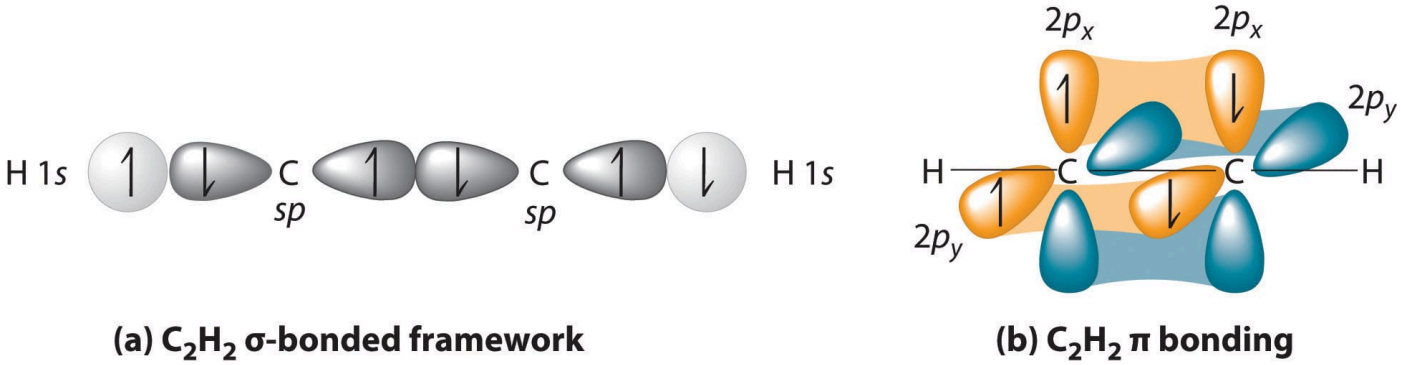


Figure 11.4.3***:*** *Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon sp hybrid orbitals and two singly occupied hydrogen 1s orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.*

Note

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 11.4.1

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:

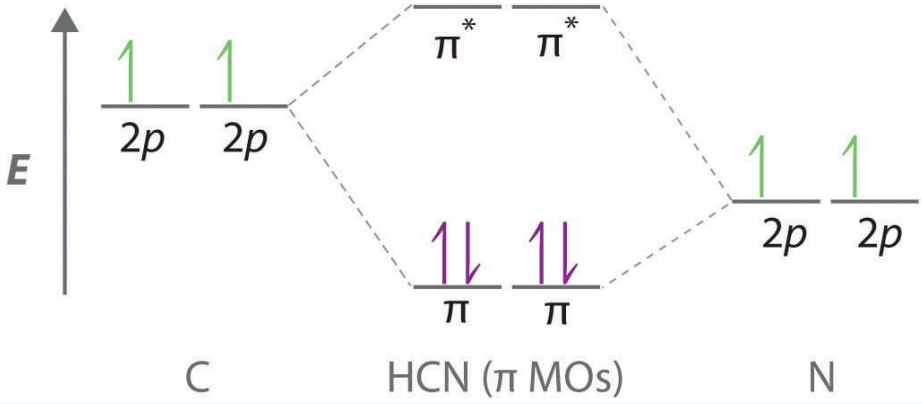
A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.
B. Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals 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

Describe the bonding in formaldehyde ($H_2C{=}O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer

- 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.

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sp Hybridization: https://youtu.be/epQXzG9WDRw

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.

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11.5: Molecular Orbital Theory

Learning Objectives

- To use molecular orbital theory to predict bond order
- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

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.

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 discussed previously, 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*:

$$\begin{aligned} MO(1) = &\quad AO(atom\ A) &+ &\quad AO(atom B) \\ MO(1) = &\quad AO(atom\ A) &- &\quad AO(atom B) \end{aligned} \tag{11.5.1}$$

The molecular orbitals created from Equation 11.5.1 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.

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 11.5.1). In a sigma (σ) orbital, 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.

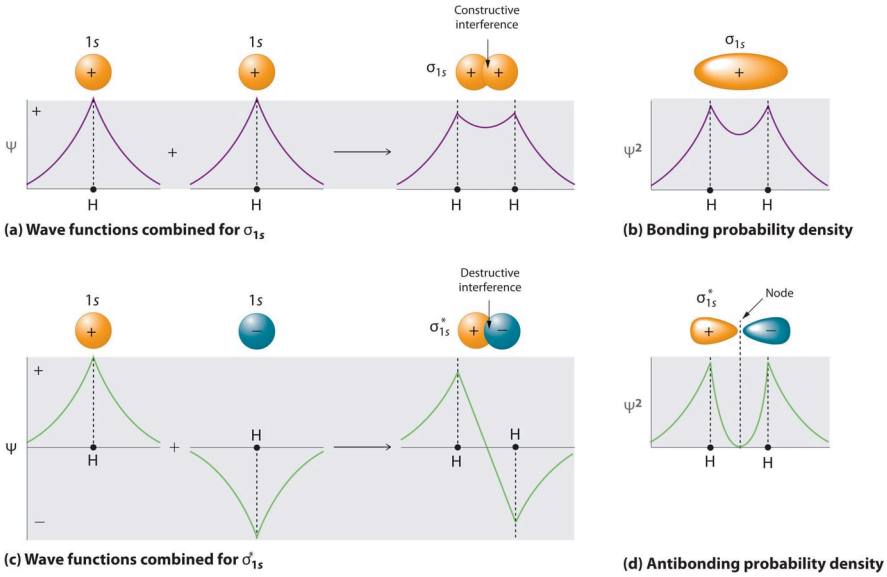


Figure 11.5.1: Molecular Orbitals for the H_2 Molecule**.** (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital 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.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{11.5.2}$$

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 11.5.1). 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:

$$\sigma^\star_{1s} \approx 1s\,(A) - 1s\,(B) \tag{11.5.3}$$

A molecule must have as many molecular orbitals as there are atomic orbitals.

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 11.5.2

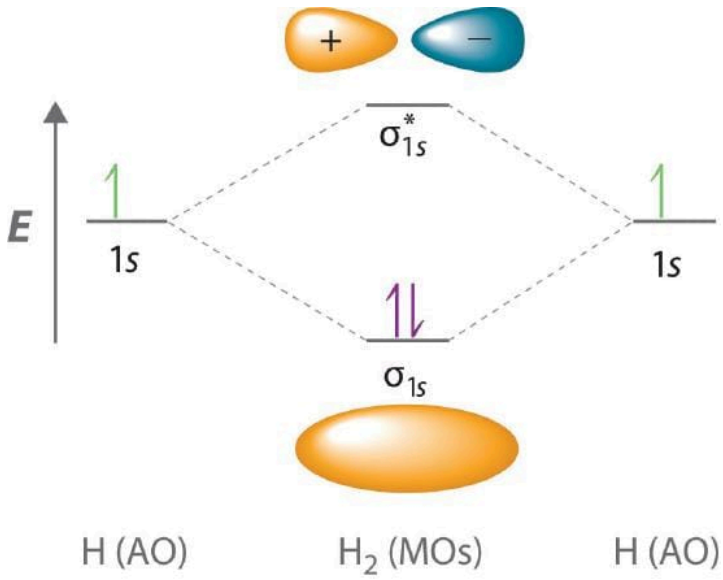


Figure 11.5.2: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1s atomic orbitals, the H_2 molecule is more 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 11.5.2). 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:

$$bond\ order = \frac{number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons}{2} \tag{11.5.4}$$

To calculate the bond order of H_2, we see from Figure 11.5.2 that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ^*_{1s} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \tag{11.5.5}$$

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 11.5.2 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.

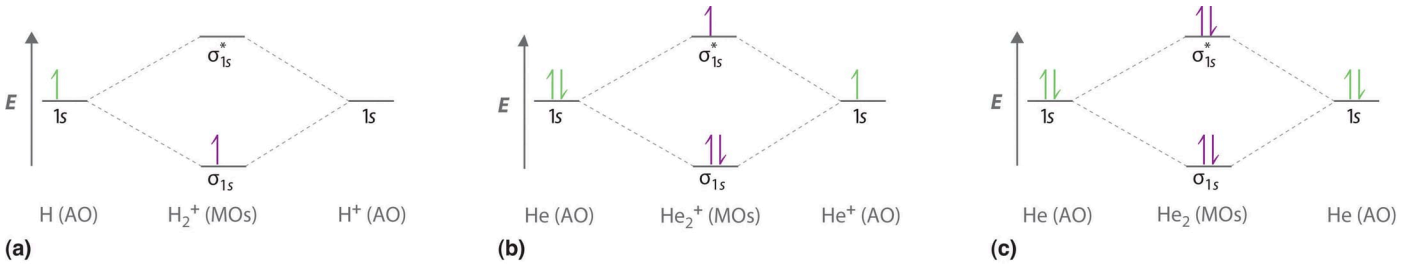


Figure 11.5.3: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure 11.5.3 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 (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 11.5.1, these predictions agree with the experimental data.

Part (b) in Figure 11.5.3 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 (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 11.5.1).

Table 11.5.1: 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. Part (c) in Figure 11.5.3 is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma^\star_{1s}$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma^\star_{1s})^1$ 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.

YouTube Video

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View this YouTube Video online

Molecular Orbital Theory: https://youtu.be/XgtOG0ezw78

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example 11.5.1

Use a molecular orbital energy-level diagram, such as those in Figure 11.5.3, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

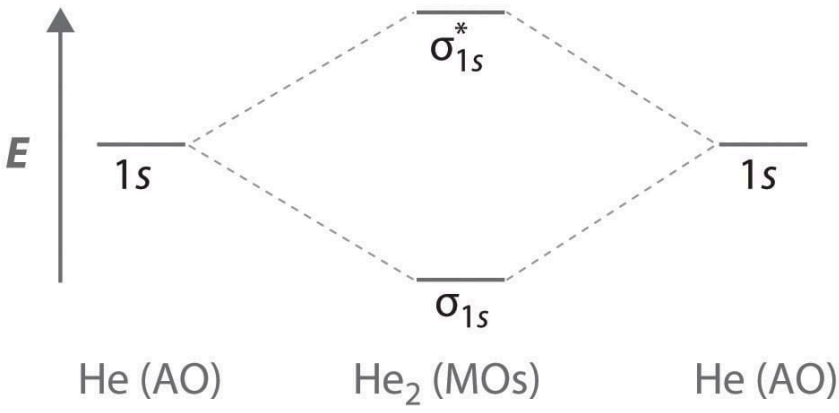
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

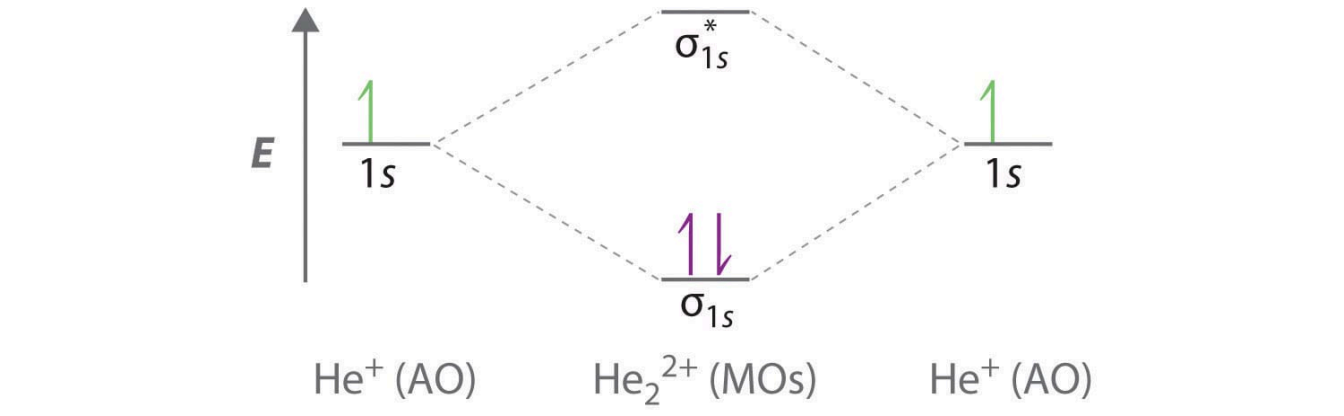
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. 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:



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 11.5.1

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 11.5.4, 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 11.5.2. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

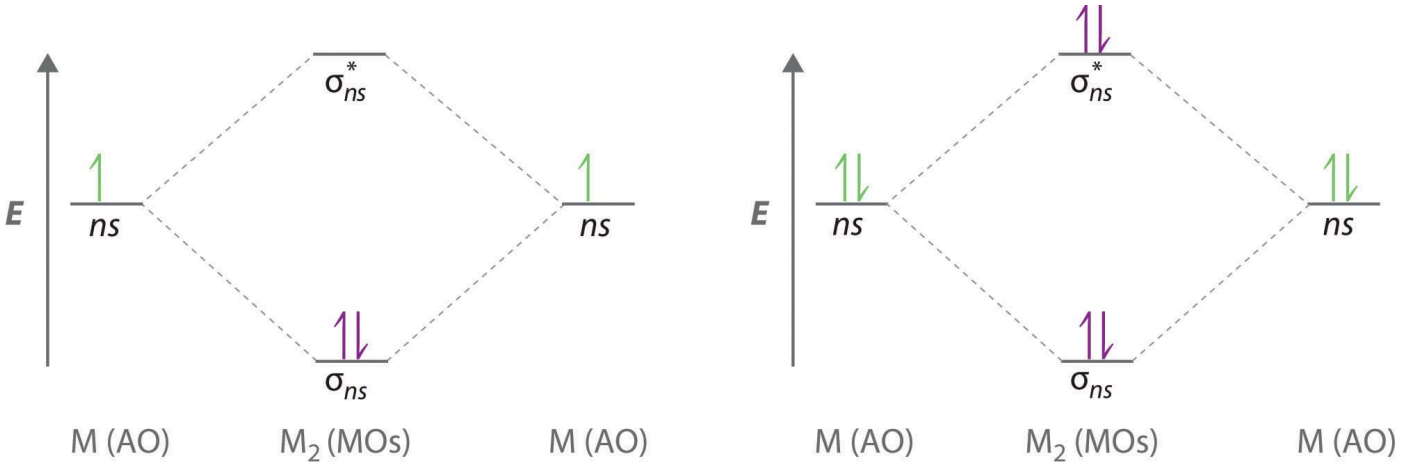


Figure 11.5.4: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. *(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic 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 11.5.3 As shown in part (b) in Figure 11.5.4, 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 11.5.2

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

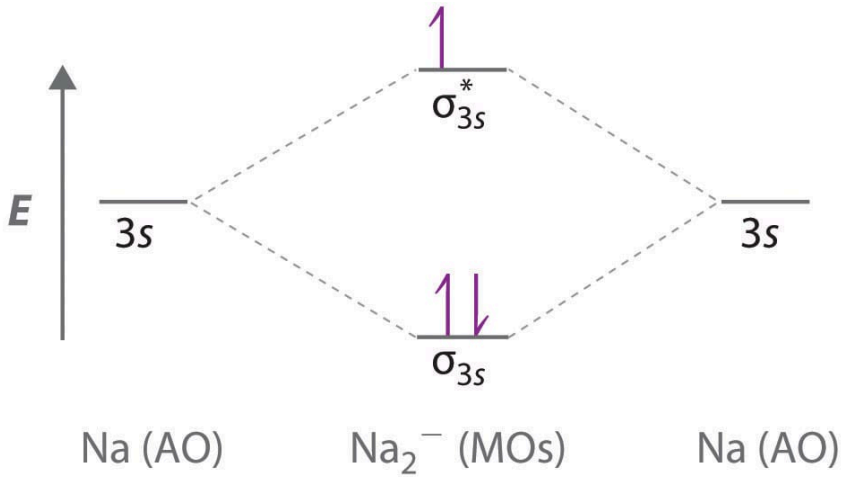
Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

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 $(\sigma_{3s})^2(\sigma^\star_{3s})^1$ 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 11.5.2

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.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{11.5.6}$$

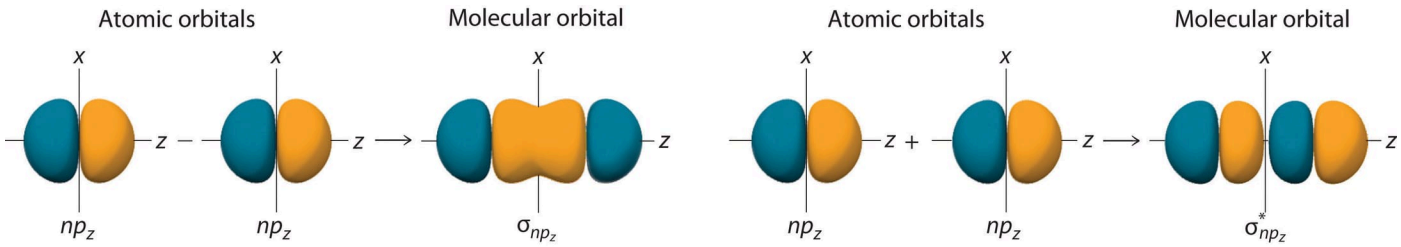
Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 11.5.5, it is the mathematical *difference* 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):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{11.5.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{11.5.8}$$

In this combination, shown in part (b) in Figure 11.5.5, 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).



(a) Bonding **(b) Antibonding**

Figure 11.5.5: 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 11.5.6, 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..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{11.5.9}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{11.5.10}$$

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.

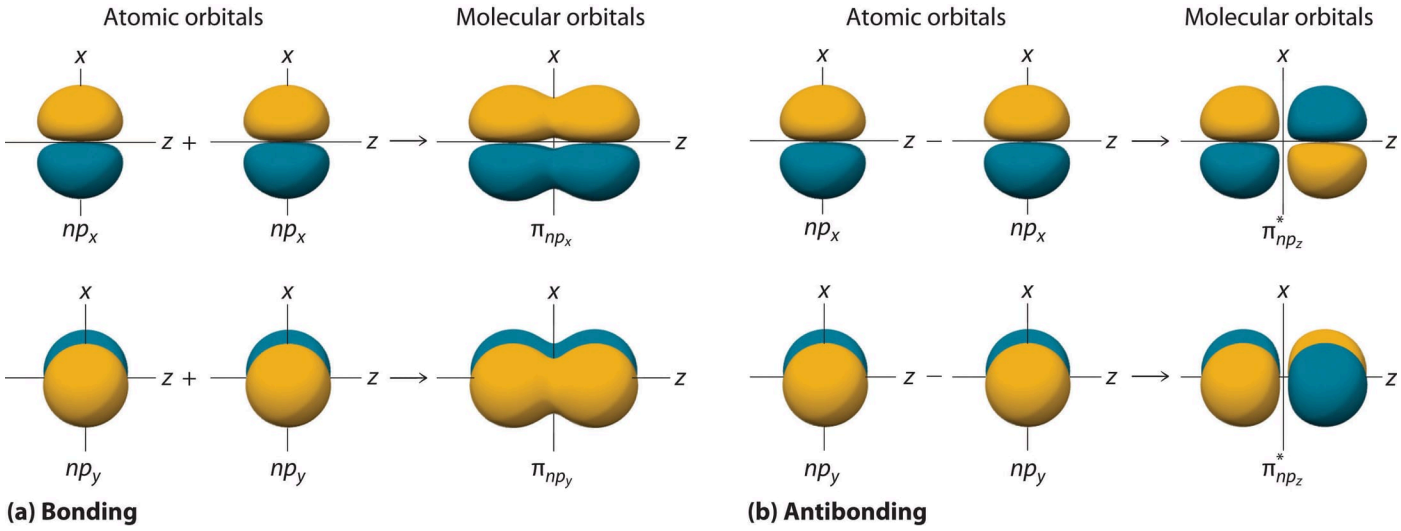


Figure 11.5.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) 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 11.5.7 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.

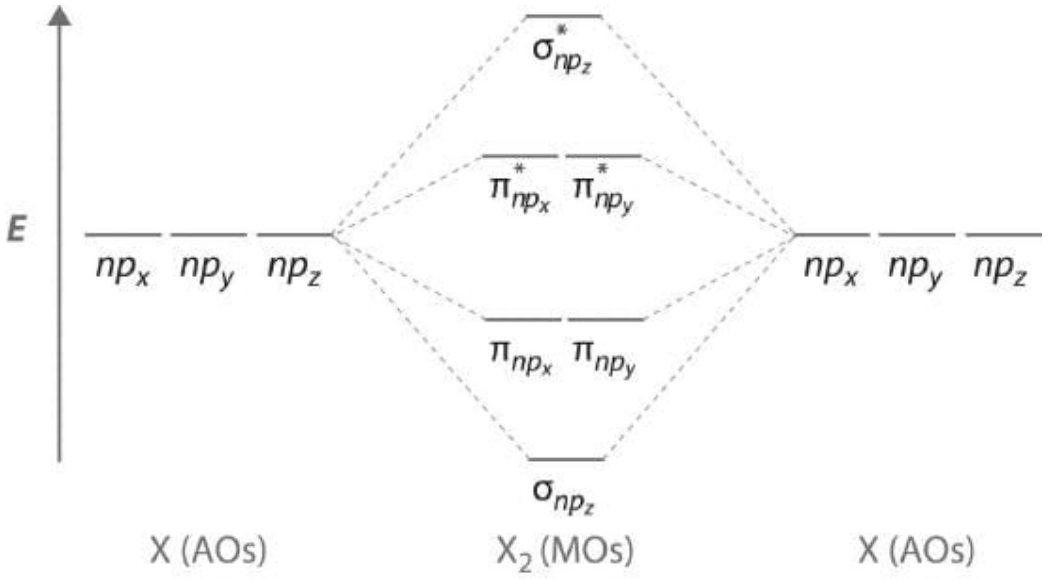
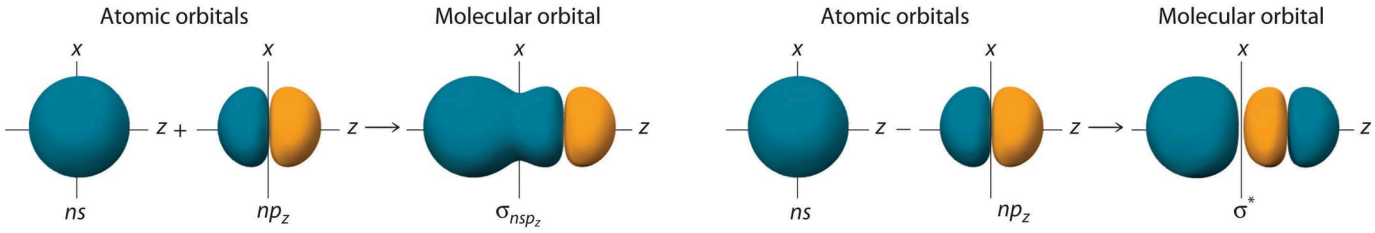


Figure 11.5.7: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals 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 11.5.8, 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.



(a) Bonding **(b) Antibonding**

Figure 11.5.8: 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.

Second Row Diatomic Molecules

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. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

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.

> The number of molecular orbitals is **always** equal to the total number of atomic orbitals we started with.

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 11.5.9; 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 $\sigma^*_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ 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.

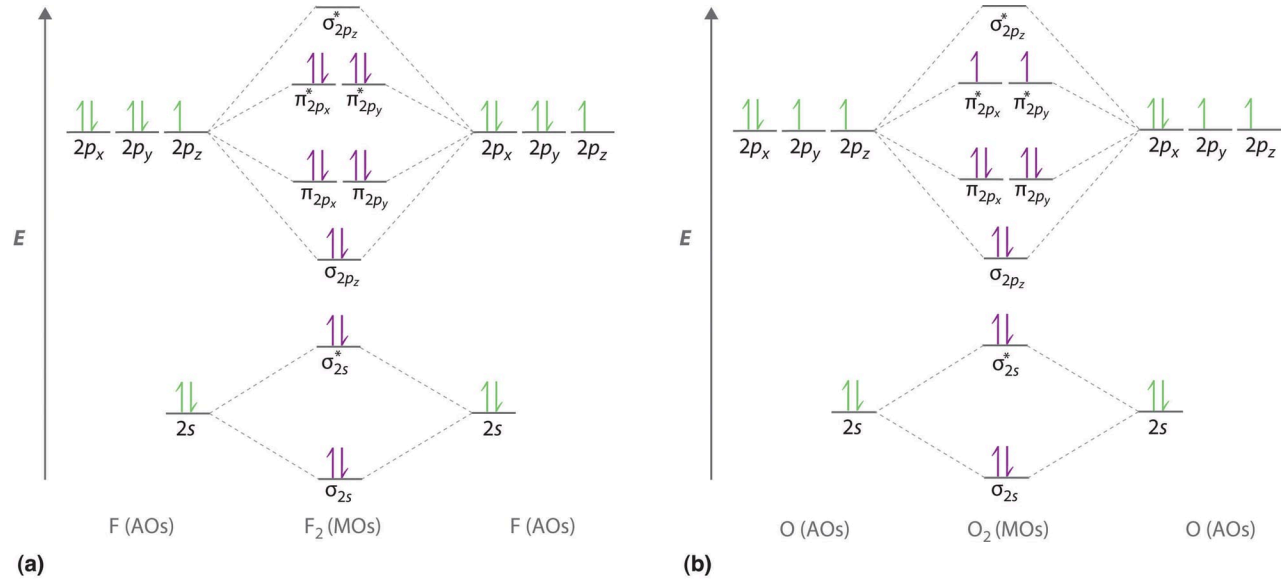


Figure 11.5.9: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, 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 $\left(\pi^*_{np_z},\ \pi^*_{np_y}\right)$ 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 11.5.9. 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 $(8 - 4) \div 2 = 2$, 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 11.5.10, 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.

View this YouTube Video online

Figure 11.5.10: 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 https://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 11.5.11 Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 11.5.11). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

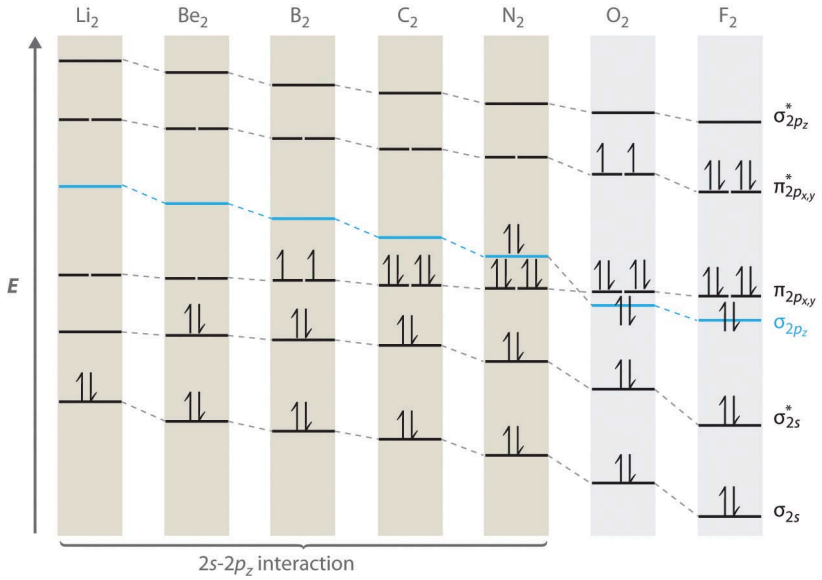


Figure 11.5.11: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. 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 11.5.3

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

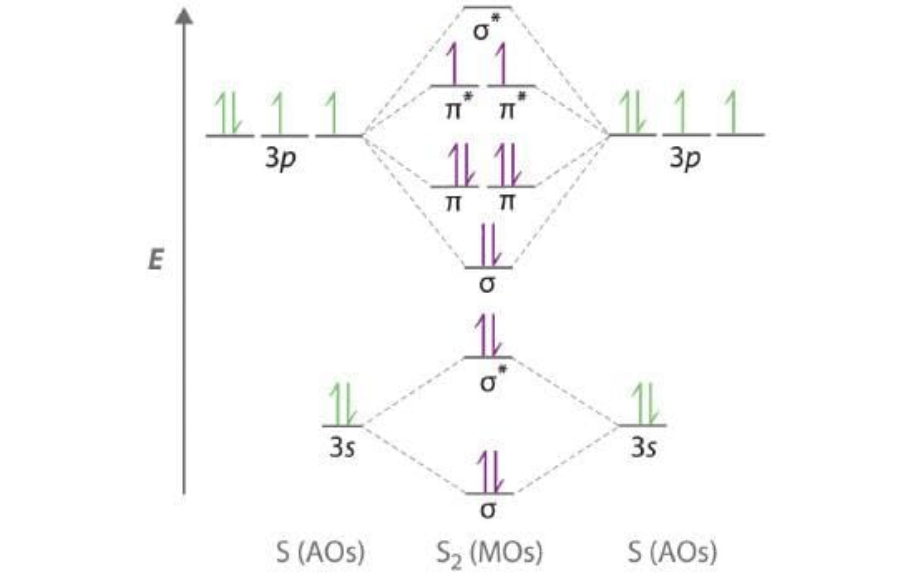
Strategy:

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 11.5.9 and Figure 11.5.11, we need to know how close in energy the 3s 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 11.5.11), 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:



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 $\pi^{\star}_{3p_x}$ and $\pi^{\star}_{3p_y}$ 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 $(\sigma_{3s})^2 (\sigma^{\star}_{3s})^2 (\sigma_{3p_z})^2 (\pi_{3p_{x,y}})^4 (\pi^{\star}_{3p_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 – 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 11.5.3

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 11.5.12. 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.

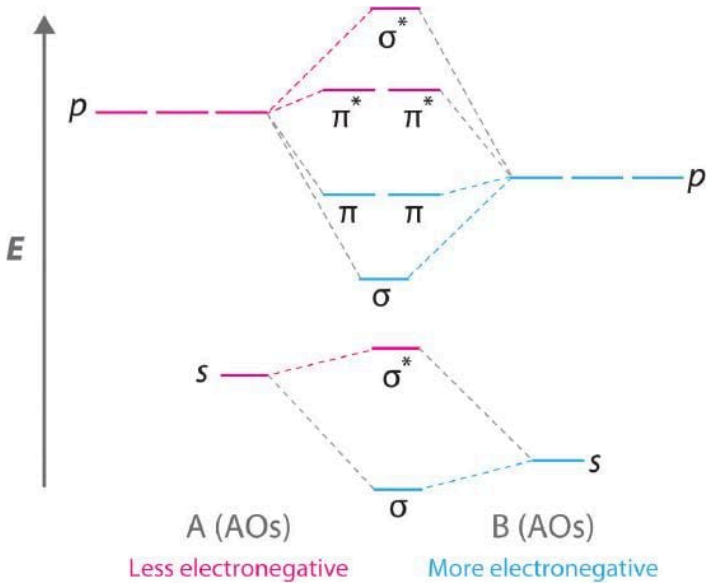


Figure 11.5.12: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally 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 11.5.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 11.5.11). 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.

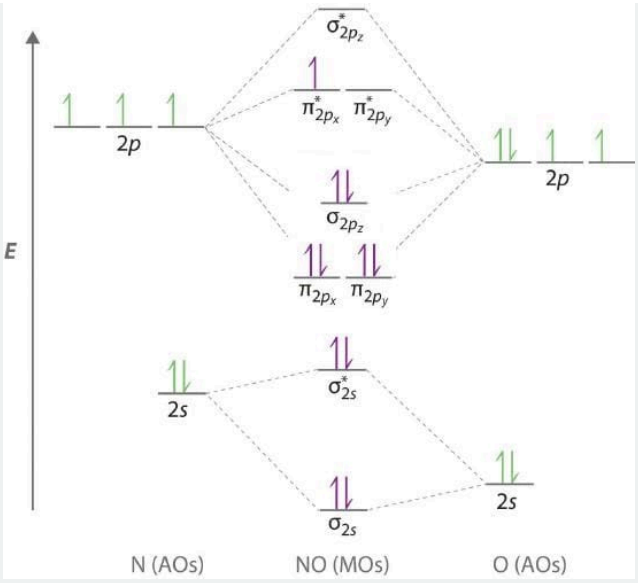


Figure 11.5.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_z},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\,(\sigma^{\star}_{2s})^2\,(\pi_{2p_{x,y}})^4\,(\sigma_{2p_z})^2\,\left(\pi^{\star}_{2p_{x,y}}\right)^2$ 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 11.5.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 11.5.13, 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.

YouTube Video

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Molecular Orbital Bonding for Second Row Elements: https://youtu.be/A_5Xa3sK_YE

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 11.5.14 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 $H^{\delta+} - -Cl^{\delta-}$.

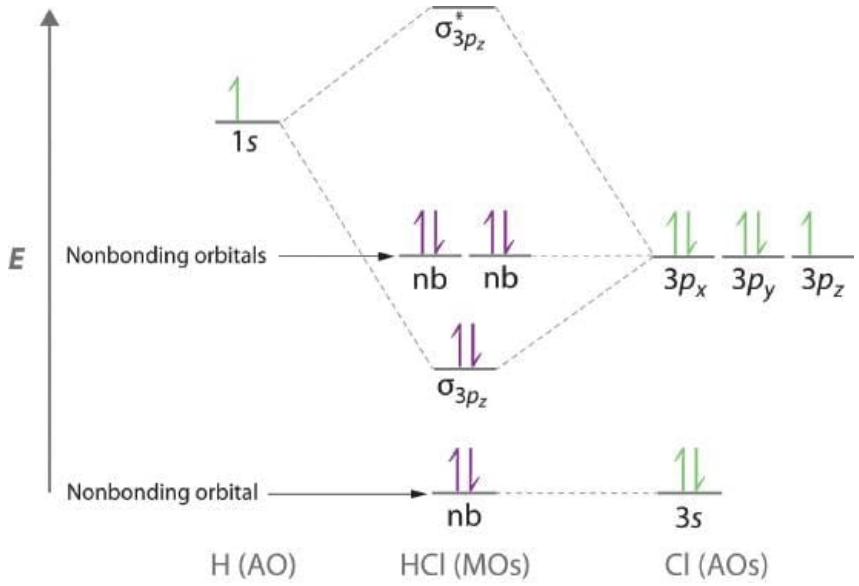


Figure 11.5.14: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

Electrons in nonbonding molecular orbitals have **no effect** on bond order.

Example 11.5.4

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 11.5.12 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

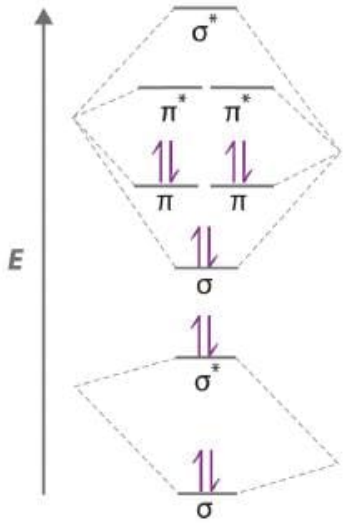
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 11.5.12 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 11.5.12 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 11.5.4

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer: All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

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.

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.

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.

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.

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 11.5.1

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 11.5.2

Ca_2^+ has a $(\sigma_{4s})^2 (\sigma^\star_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

Exercise 11.5.3

$(\sigma_{2s})^2 (\sigma^\star_{2s})^2 (\sigma_{2p_z})^2 (\pi_{2p_{x,y}})^4 (\pi_{2p^\star_{x,y}})^4$

bond order of 1;

no unpaired electrons

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11.6: Delocalized Electrons: Bonding in the Benzene Molecule

Learning Objectives

- To be able to explain how mixing atomic orbitals make molecule orbitals with delocalized bonding

The advantage of MO theory becomes more apparent when we think about π bonds, especially in those situations where two or more π bonds are able to interact with one another. Let's first consider the π bond in ethene from an MO theory standpoint (in this example we will be disregarding the various sigma bonds, and thinking *only* about the π bond). According to MO theory, the two atomic $2p_z$ orbitals combine to form two π **molecular orbitals**, one a low-energy π bonding orbital and one a high-energy **π-star (π*) antibonding molecular orbital**. These are sometimes denoted in molecular diagrams with the Greek letter psi (Ψ) instead of π (Figure 11.6.1).

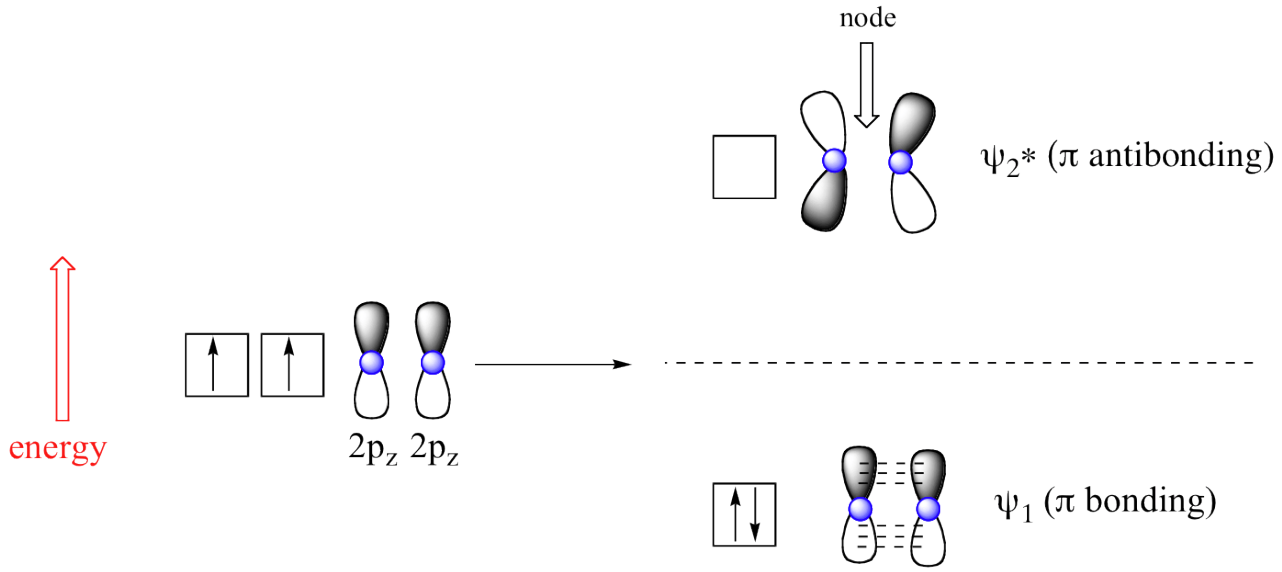


Figure 11.6.1: Mixing of adjacent p atomic orbitals results in the bonding (π) and anti-bonding (π^*) molecular orbitals.

In the bonding Ψ_1 orbital, the two shaded lobes of the $2p_z$ orbitals interact constructively with each other, as do the two unshaded lobes (remember, the shading choice represents mathematical (+) and (-) signs for the wavefunction). Therefore, there is increased electron density between the nuclei in the molecular orbital – this is why it is a bonding orbital. In the higher-energy antibonding Ψ_2^* orbital, the shaded lobe of one $2p_z$ orbital interacts destructively with the unshaded lobe of the second $2p_z$ orbital, leading to a node between the two nuclei and overall repulsion.

By the *aufbau* principle, the two electrons from the two atomic orbitals will be paired in the lower-energy Ψ_1 orbital when the molecule is in the ground state (Figure 11.6.1).

Now, consider the 1,3-butadiene molecule. From valence orbital theory we might expect that the C_2-C_3 bond in this molecule, because it is a σ bond that would rotate freely.

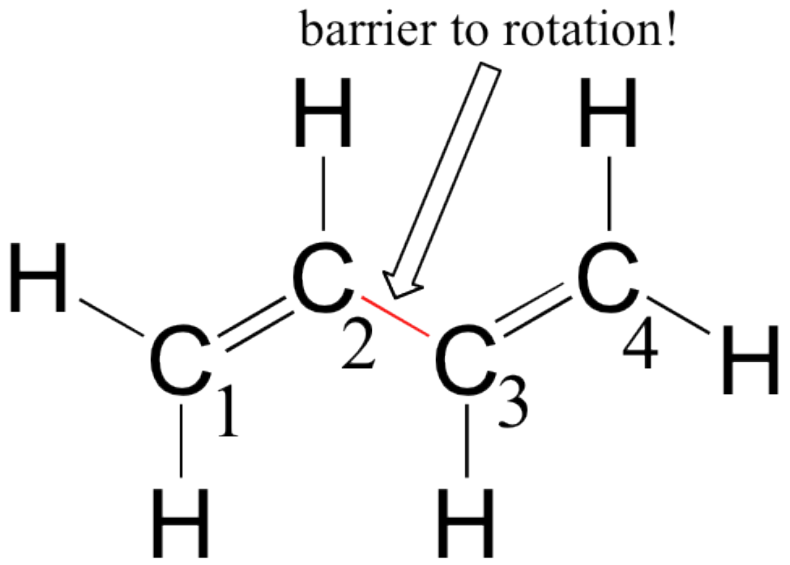


Figure 11.6.2: The "single bond" in the 1,3-butadiene molecule is expected to rotate just like all sigma bonds.

However, it is experimentally found that there are significant barriers to rotation about this bond (as well as about the C_1-C_2 and C_3-C_4 double bonds), and that the entire molecule is planar. It is also observed that the C_2-C_3 bond, while longer than the C_1-C_2 and C_3-C_4 double bonds, is significantly shorter than a typical carbon-carbon single bond.

Molecular orbital theory accounts for these observations with the concept of **delocalized π bonds**. In this picture, the four $2p_z$ orbitals are all parallel to each other (and perpendicular to the plane of the σ bonds), and thus there is π-overlap not just between C_1 and C_2 and C_3 and C_4, but between C_2 and C_3 as well. The four atomic ($2p_z$) orbitals have combined to form four π molecular orbitals.

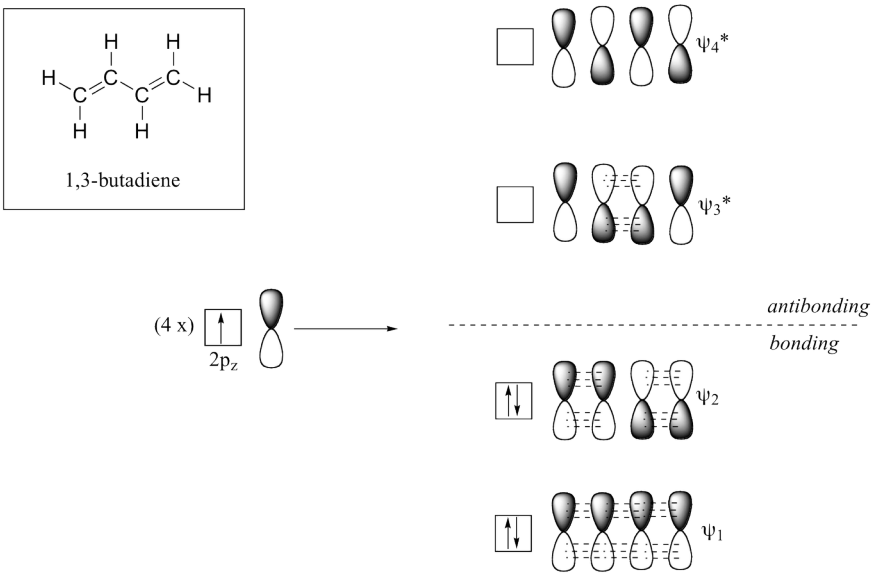


Figure 11.6.3: Molecular orbitals expected for mixing of the perpendicular p atomic orbitals of the 1,3-butadiene molecule.

The lowest energy molecular orbital, Ψ_1, has zero nodes, and is a bonding MO. Slightly higher in energy, but still lower than the isolated *p* orbitals, is the Ψ_2 orbital. This orbital has one node between C_2 and C_3, but is still a bonding orbital due to the two constructive interactions between C_1-C_2 and C_3-C_4. The two higher-energy MO's are denoted Ψ_3* and Ψ_4*, and are antibonding. Notice that Ψ_3* has two nodes and one constructive interaction, while Ψ_4* has three nodes and zero constructive interactions. The energy of both of these antibonding molecular orbitals is higher than that of the $2p_z$ atomic orbitals of which they are composed.

By the *aufbau* principle, the four electrons from the isolated $2p_z$ atomic orbitals are placed in the bonding $\Psi_1$and Ψ_2 MO's. Because $\Psi_1$includes constructive interaction between C_2 and C_3, there is a degree, in the 1,3-butadiene molecule, of π-bonding interaction between these two carbons, which accounts for the shorter length and the barrier to rotation. The simple Lewis structure picture of 1,3-butadiene shows the two π bonds as being isolated from one another, with each pair of π electrons 'stuck' in its own π bond. However, molecular orbital theory predicts (accurately) that the four π electrons are to some extent delocalized, or 'spread out', over the whole π system.

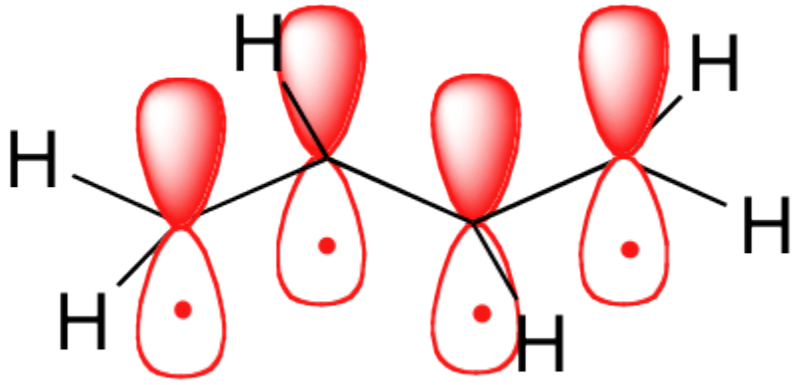
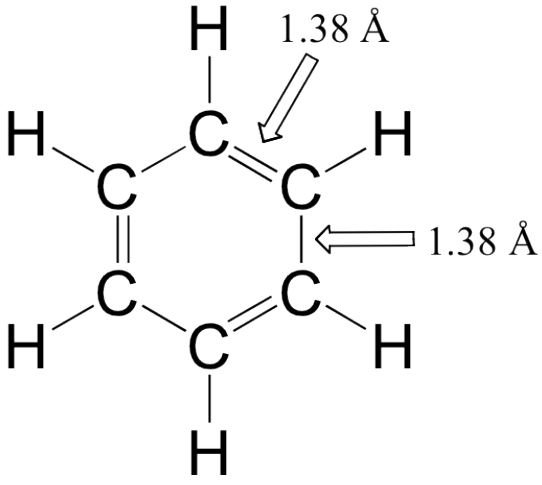


Figure 11.6.3: The atomic orbitals that combine to generate the lowest energy molecular orbital in *the 1,3-butadiene molecule*.

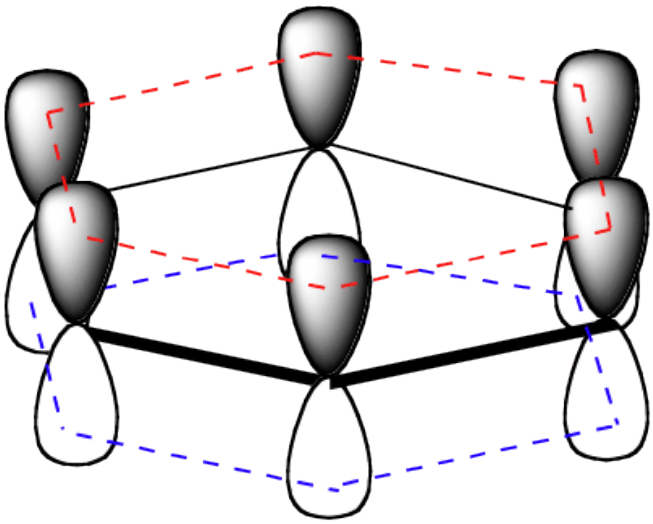
1,3-butadiene is the simplest example of a system of '**conjugated'** π bonds. To be considered conjugated, two or more π bonds must be separated by only one single bond – in other words, there cannot be an intervening sp^3-hybridized carbon, because this would break up the overlapping system of parallel $2p_z$ orbitals.

Benzene

Molecular orbital theory is especially helpful in explaining the unique properties of a class of compounds called aromatics. Benzene, a common organic solvent, is the simplest example of an aromatic compound. Although benzene is most often drawn with three double bonds and three single bonds (Figure 11.6.4), it is known that all of the carbon-carbon bonds in benzene are exactly the same length - 1.38 Å. This is shorter than a typical carbon-carbon single bond (about 1.54 Å), and slightly longer than a typical carbon-carbon double bond (about 1.34 Å).



benzene



π electrons delocalized around the ring, above and below the plane

Figure 11.6.4: (left(Simplified and incorrect three-doube bond/three single bond picture of bonding benzene. (right) The (2p_z\) atomic orbitals of the carbons overlap strongly above and below the ring.

Benzene is also a *cyclic* molecule in which all of the ring atoms are sp^2-hybridized that allows the π electrons to be delocalized in molecular orbitals that extend all the way around the ring, above and below the plane of the ring. For this to happen, of course, the ring must be planar – otherwise the $2p_z$ orbitals could not overlap properly. Benzene was experimentally confirmed to be flat molecule by Dame Kathleen Londsale with X-ray crystallography.

As shown in Figure 11.6.5, the cyclic array of six \2P_z\)-orbitals (one on each carbon) overlap to generate six molecular orbitals, three bonding and three antibonding. The plus and minus signs shown in the diagram do not represent electrostatic charge, but refer to phase signs in the equations that describe these orbitals (in the diagram the phases are also color coded). When the phases correspond, the orbitals overlap to generate a common region of like phase, with those orbitals having the greatest overlap (e.g. π_1) being lowest in energy. The remaining carbon valence electrons then occupy these molecular orbitals in pairs, resulting in a fully occupied (6 electrons) set of bonding molecular orbitals.

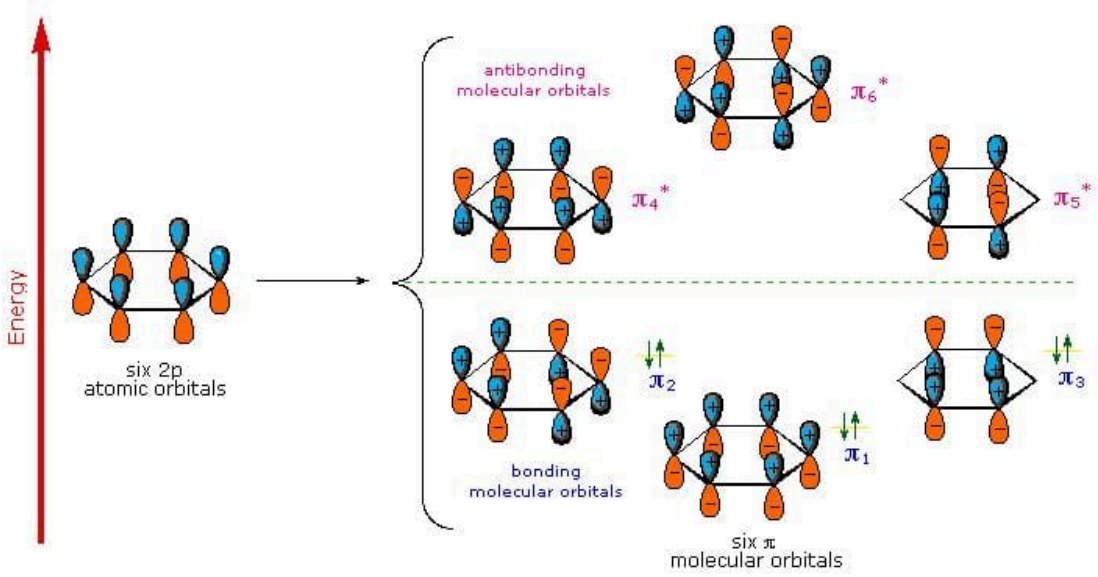


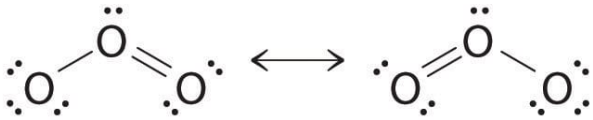
Figure 11.6.5: The Molecular Orbitals of Benzene.

Aromaticity

It is this completely filled set of bonding orbitals, or **closed shell**, that gives the benzene ring its thermodynamic and chemical stability, just as a filled valence shell octet confers stability on the inert gases. This added stability is call *aromaticity*. and is discuss in more detail in organic chemistry courses.

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^-). We showed that 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 11.6.6. 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.

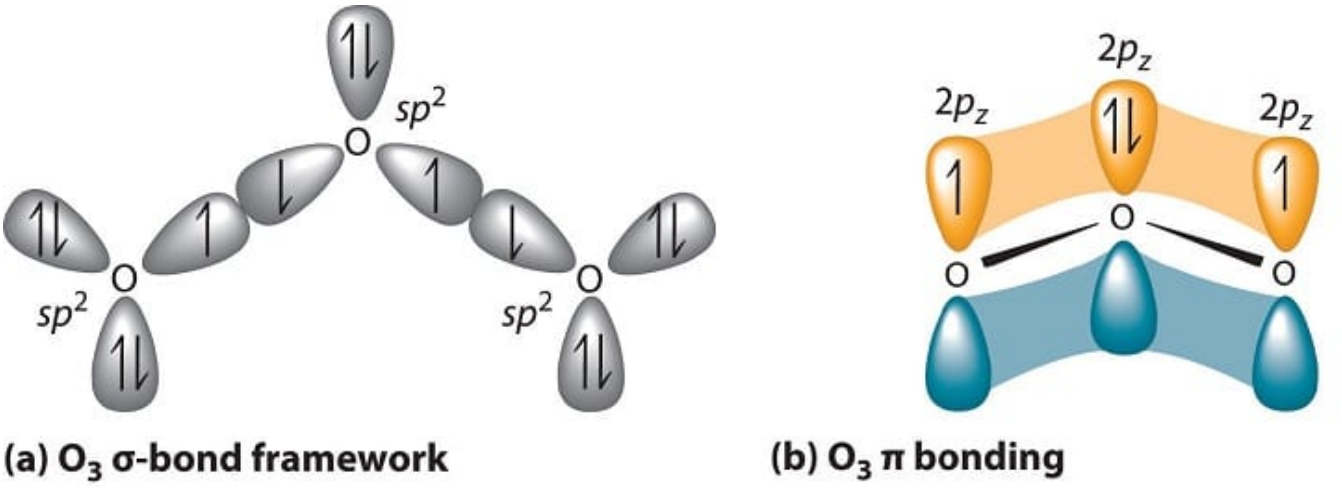


Figure 11.6.6: Bonding in Ozone. (a) In the formation of the σ-bonded framework, three sets of oxygen sp^2 hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O_3. (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 $2p$ atomic orbitals give us three molecular orbitals, as shown in Figure 11.6.7. 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; it is a nonbonding molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

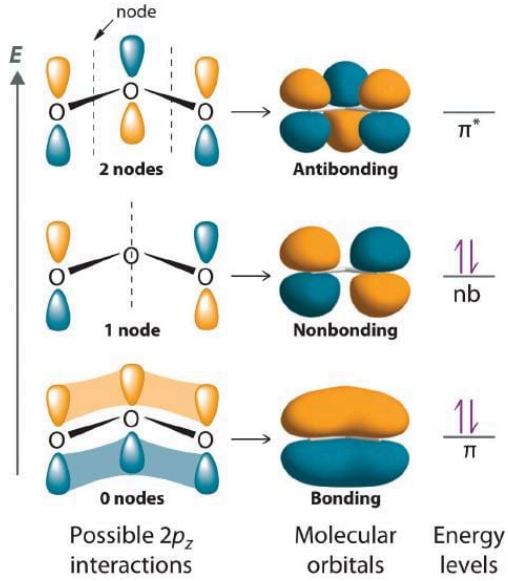


Figure 11.6.7: π Bonding in Ozone. The three unhybridized 2pz atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π^* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this diagram fills 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 11.6.7, 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 approach, however, 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. 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 11.6.1

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

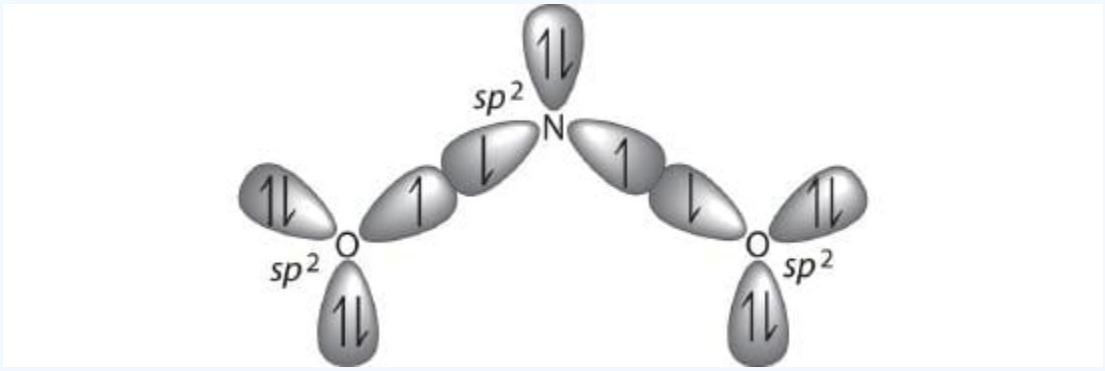
Strategy:

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.

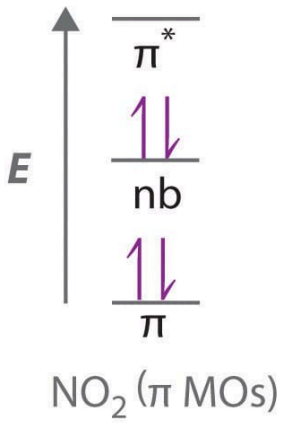
Solution:

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 11.6.1

Describe the bonding in the formate ion (HCO_2^-), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

Answer

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 $frac32$

The Chemistry of Vision

Hydrocarbons in which two or more carbon–carbon double bonds are directly linked by carbon–carbon single bonds 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 $11.6.8$. 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 $11.6.9$). 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.

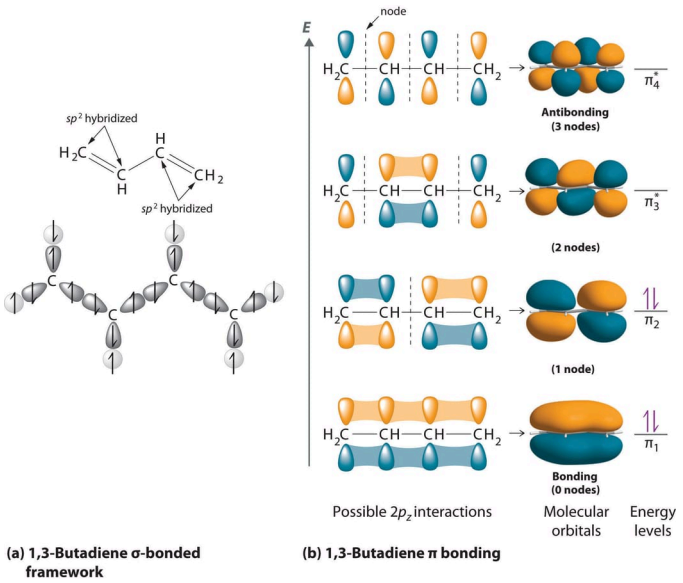


Figure 11.6.8: π Bonding in 1,3-Butadiene. (a) If each carbon atom is assumed to be sp^2 hybridized, we can construct a σ-bonded framework that accounts for the C–H and C–C single bonds, leaving *four* singly occupied $2p_z$ orbitals, one on each carbon atom. (b) As in ozone, these orbitals can interact, 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.

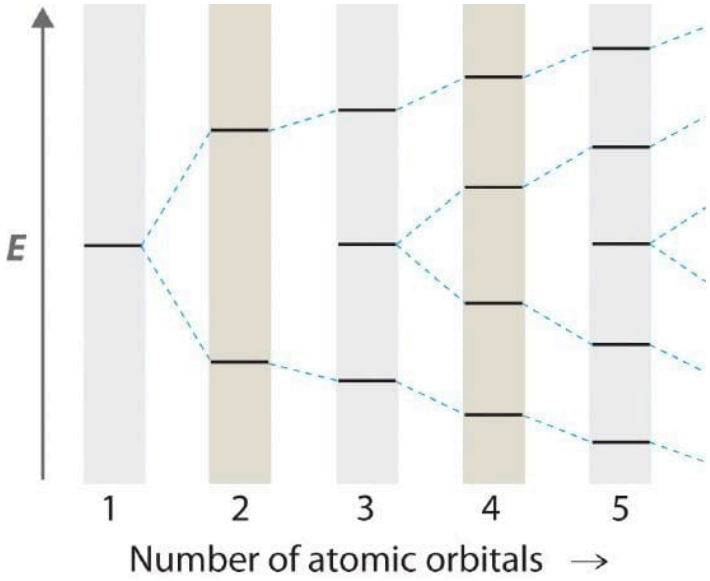


Figure 11.6.9 Molecular Orbital Energy-Level Diagrams for a Chain of n Like Orbitals That Interact ($n \leq 5$).

> 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.

Delocalization

Delocalization is central feature of molecular orbital theory where rather than the lone pair of electrons contained in localize bonds (as in the valence bond theory), electrons can exist in *molecular orbitals* that are spread over the entire molecule.

Summary

The 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.

Contributors and Attributions

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11.7: Bonding in Metals

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 11.7.1 shows the pattern of molecular orbitals that results from the interaction of ns orbitals as n increases from 2 to 5.

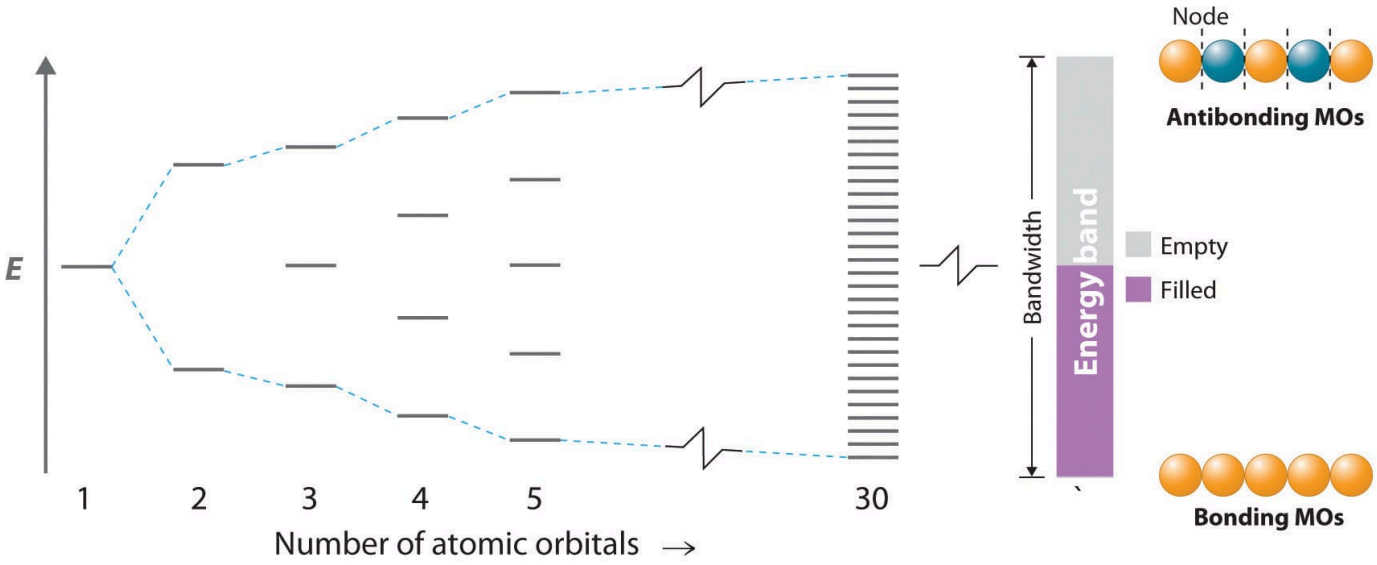


Figure 11.7.1: The Molecular Orbital Energy-Level Diagram for a Linear Arrangement of n Atoms, Each of Which Contains a Singly Occupied s Orbital. As n becomes very large, the energy separation between adjacent levels becomes so small that a single continuous band of allowed energy levels results. The 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 11.7.1, 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 11.7.1 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 11.7.1 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 11.7.1, 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 11.7.2). 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.

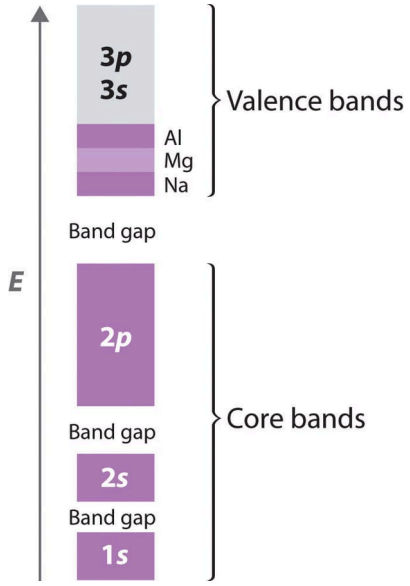


Figure 11.7.2: The Band Structures of the Period 3 Metals Na, Mg, and Al. The 3s and 3p valence bands overlap in energy to form a continuous set of energy levels that can hold a maximum of eight electrons per atom.

Because they extend farther from the nucleus, the valence orbitals of adjacent atoms (3s and 3p in Figure 11.7.2) 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 11.7.2. 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 11.7.3a. 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.

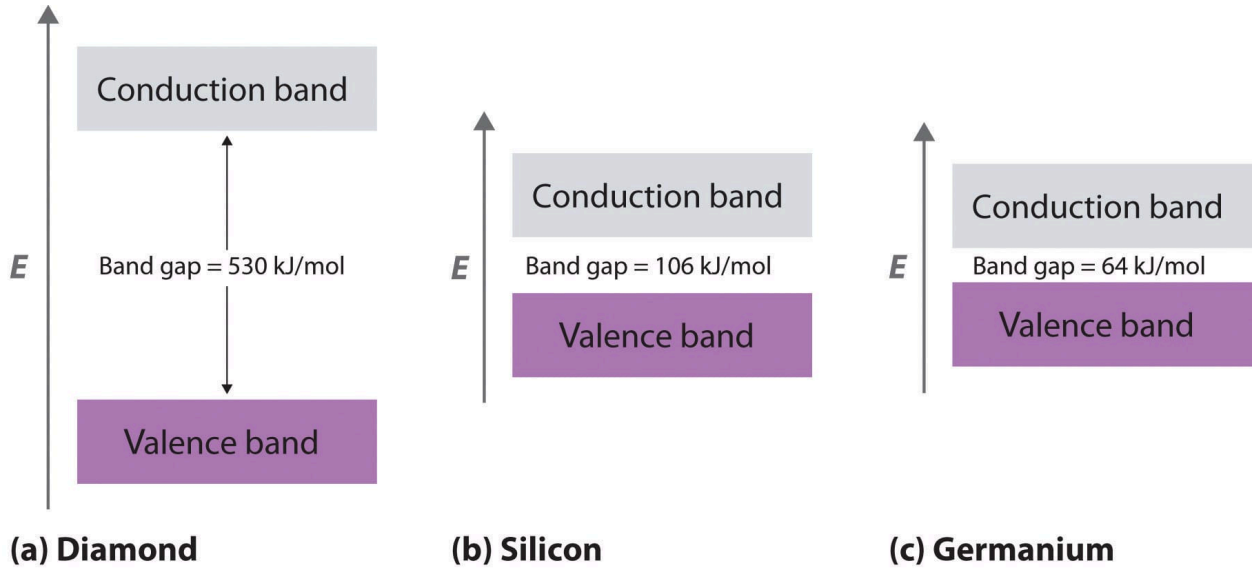


Figure 11.7.2: Energy-Band Diagrams for Diamond, Silicon, and Germanium. The band gap gets smaller from C to Ge.

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 11.7.2). 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 11.7.4).

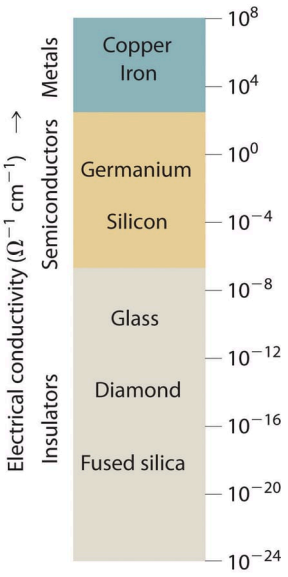


Figure 11.7.4: A Logarithmic Scale Illustrating the Enormous Range of Electrical Conductivities of Solids

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 11.7.5.

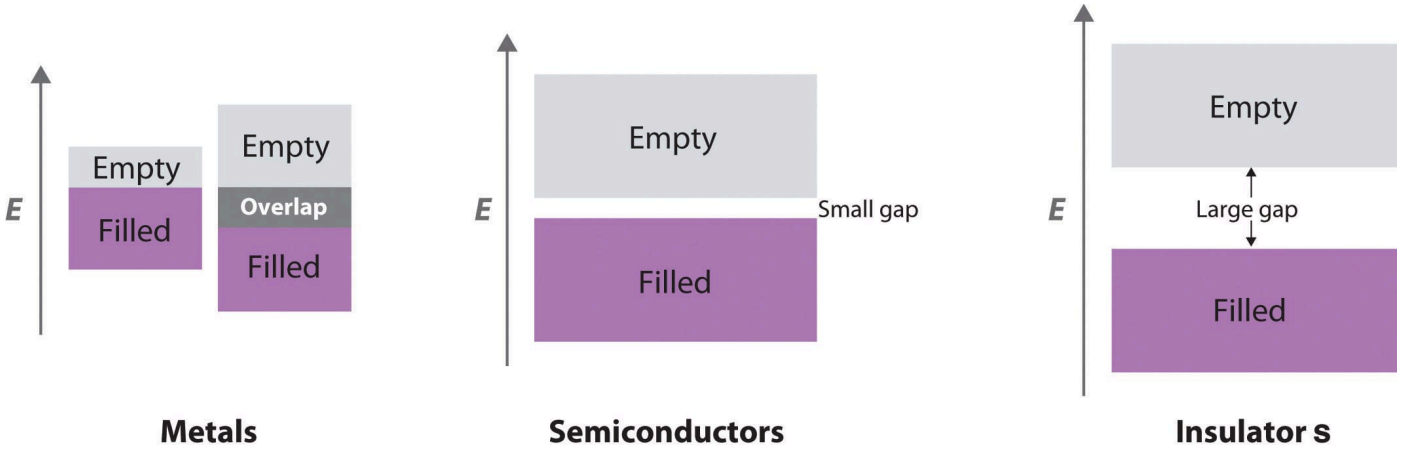


Figure 11.7.5: A Comparison of the Key Features of the Band Structures of Metals, Semiconductors, and Insulators. Metallic behavior can arise either from the presence of a single partially filled band or from two overlapping bands (one full and one empty).

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 11.7.6.

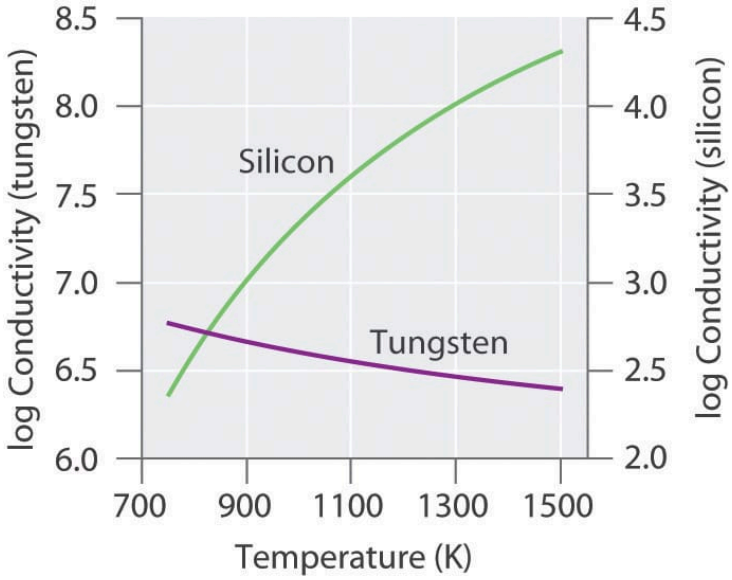


Figure 11.7.6: The Temperature Dependence of the Electrical Conductivity of a Metal versus a Semiconductor. The conductivity of the metal (tungsten) decreases relatively slowly with increasing temperature, whereas the conductivity of the semiconductor (silicon) increases much more rapidly.

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 11.7.7*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).

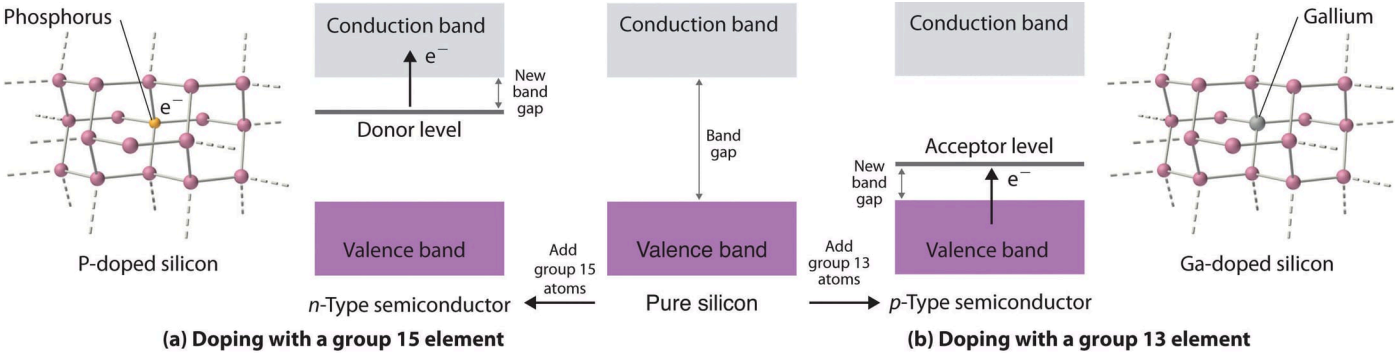


Figure 11.7.7: Structures and Band Diagrams of n-Type and p-Type Semiconductors. (a) Doping silicon with a group 15 element results in a new filled level between the valence and conduction bands of the host. (b) Doping silicon with a group 13 element results in a new empty level between the valence and 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 11.7.7*b*, adding an impurity such as gallium to a silicon crystal creates isolated electron-deficient sites in the host lattice.

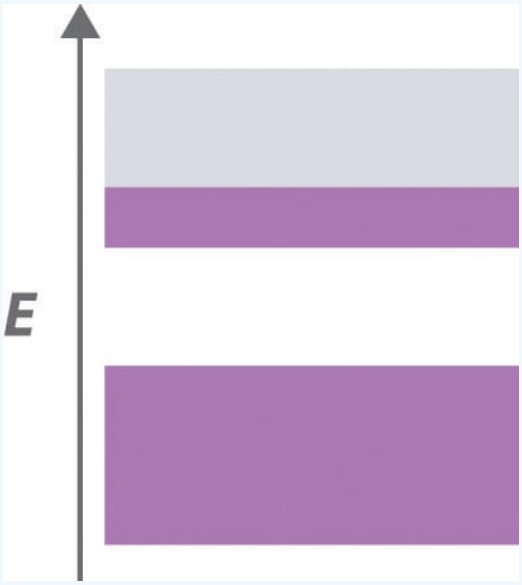
The electronic energy of these empty sites also lies between those of the filled valence band and the empty conduction band of the host but much closer to the filled valence band. It is therefore relatively easy to excite electrons from the valence band of the host to the isolated impurity atoms, thus 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 11.7.1

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:

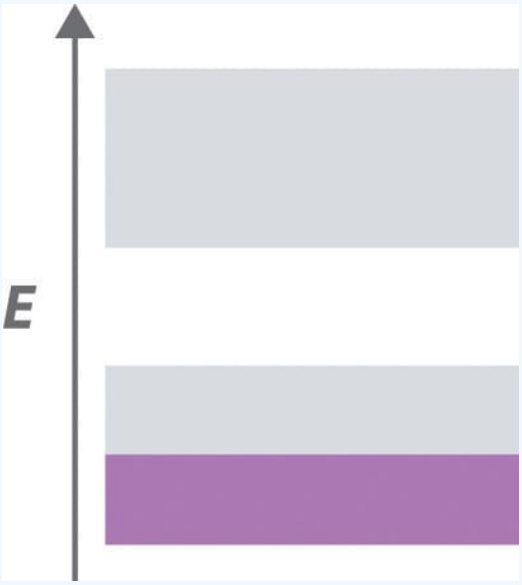
A. Based on the occupancy of the lower and upper bands, predict whether the substance will be an electrical conductor. Then predict how its conductivity will change with temperature.
B. After all the electrons are removed from the upper band, predict how the band gap would affect the electrical properties 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 11.7.1

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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11.8: Some Unresolved Issues

under construction

The breakdown of d-orbital hybridization

SF6 etc.

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11.E: Chemical Bonding II: Additional Aspects (Exercises)

11.7 Bonding in Metals

Conceptual Problems

1. Can band theory be applied to metals with two electrons in their valence s orbitals? with no electrons in their valence s orbitals? Why or why not?
2. Given a sample of a metal with 10^{20} atoms, how does the width of the band arising from p orbital interactions compare with the width of the band arising from s orbital interactions? from d orbital interactions?
3. Diamond has one of the lowest electrical conductivities known. Based on this fact, do you expect diamond to be colored? Why? How do you account for the fact that some diamonds are colored (such as “pink” diamond or “green” diamond)?
4. Why do silver halides, used in the photographic industry, have band gaps typical of semiconducting materials, whereas alkali metal halides have very large band gaps?
5. As the ionic character of a compound increases, does its band gap increase or decrease? Why?
6. Why is silicon, rather than carbon or germanium, used in the semiconductor industry?
7. Carbon is an insulator, and silicon and germanium are semiconductors. Explain the relationship between the valence electron configuration of each element and their band structures. Which will have the higher electrical conductivity at room temperature—silicon or germanium?
8. How does doping affect the electrical conductivity of a semiconductor? Draw the effect of doping on the energy levels of the valence band and the conduction band for both an n-type and a p-type semiconductor.

Answers

3. The low electrical conductivity of diamond implies a very large band gap, corresponding to the energy of a photon of ultraviolet light rather than visible light. Consequently, diamond should be colorless. Pink or green diamonds contain small amounts of highly colored impurities that are responsible for their color.
4. -
5. As the ionic character of a compound increases, the band gap will also increase due to a decrease in orbital overlap. Remember that overlap is greatest for orbitals of the same energy, and that the difference in energy between orbitals on adjacent atoms increases as the difference in electronegativity between the atoms increases. Thus, large differences in electronegativity increase the ionic character, decrease the orbital overlap, and increase the band gap.

Numerical Problems

1. Of Ca, N, B, and Ge, which will convert pure silicon into a p-type semiconductor when doping? Explain your reasoning.
2. Of Ga, Si, Br, and P, which will convert pure germanium into an n-type semiconductor when doping? Explain your reasoning.

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12: INTERMOLECULAR FORCES: LIQUIDS AND SOLIDS

Petrucci: *General Chemistry*
Principles and Modern Applications

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12.1: Intermolecular Forces
12.2: Some Properties of Liquids
12.3: Some Properties of Solids
12.4: Phase Diagrams
12.5: Network Covalent Solids and Ionic Solids
12.6: Crystal Structures
12.7: Energy Changes in the Formation of Ionic Crystals

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12.1: 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 $12.1.1a$.

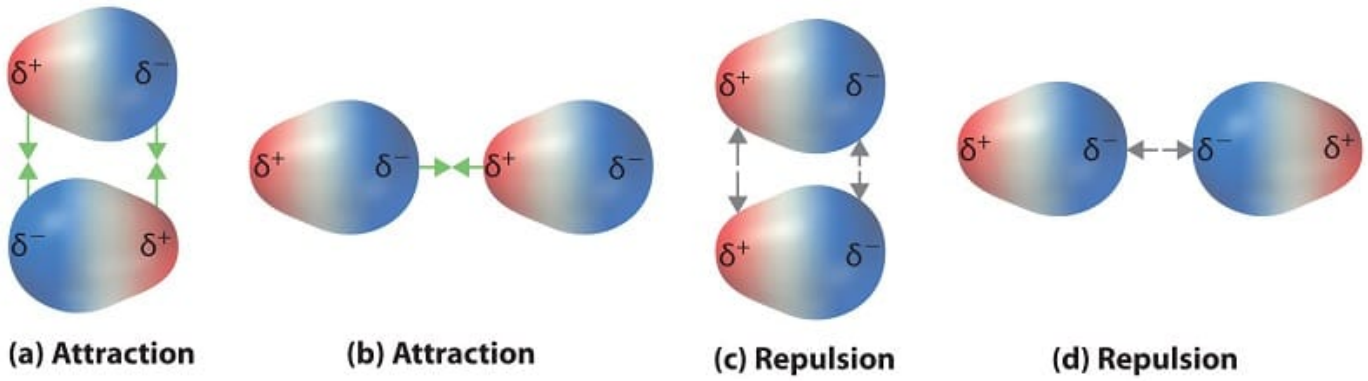


Figure 12.1.1: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or 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 12.1.1*c*). Hence dipole–dipole interactions, such as those in Figure 12.1.1*b*, are *attractive intermolecular interactions*, whereas those in Figure 12.1.1*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 12.1.2. On average, however, the attractive interactions dominate.

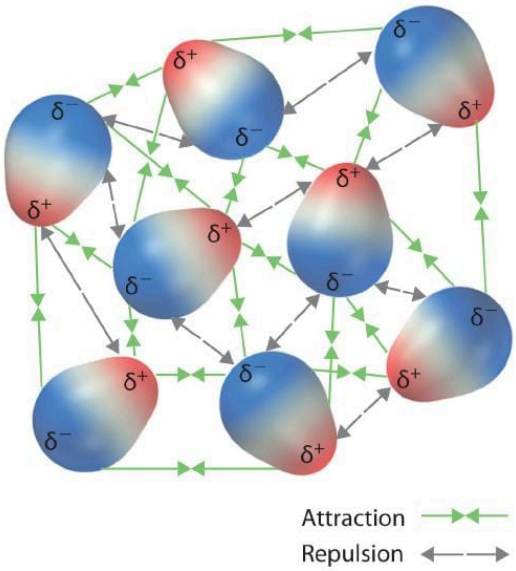


Figure 12.1.2: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules. (CC BY-SA-NC; anonymous)

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 12.1.1.

Table 12.1.1: 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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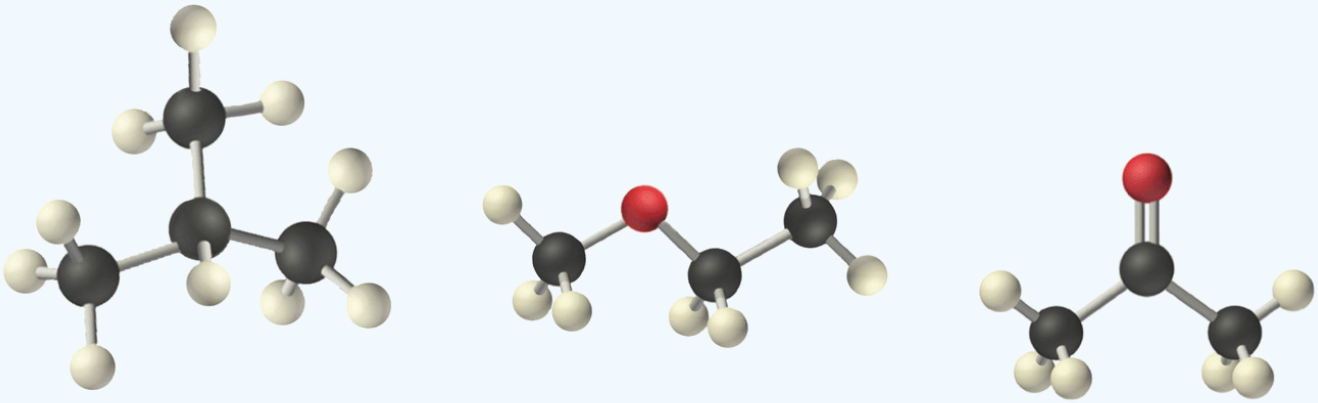
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Video Discussing Dipole Intermolecular Forces. Source: Dipole Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 12.1.1

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 12.1.1

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 12.1.2).

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 12.1.2: 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 12.1.3, 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.

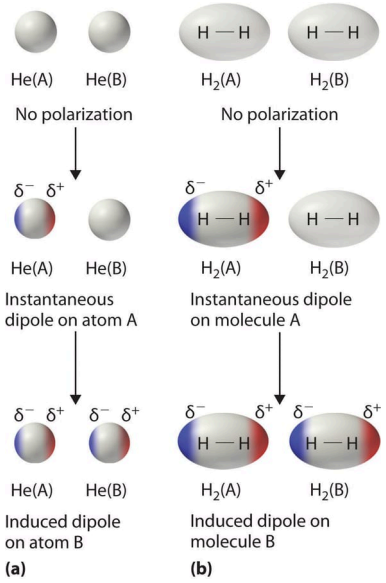


Figure 12.1.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

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 12.1.3, tends to become more pronounced as atomic and molecular masses increase (Table 12.1.2). 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 12.1.4). 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 12.1.4 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).

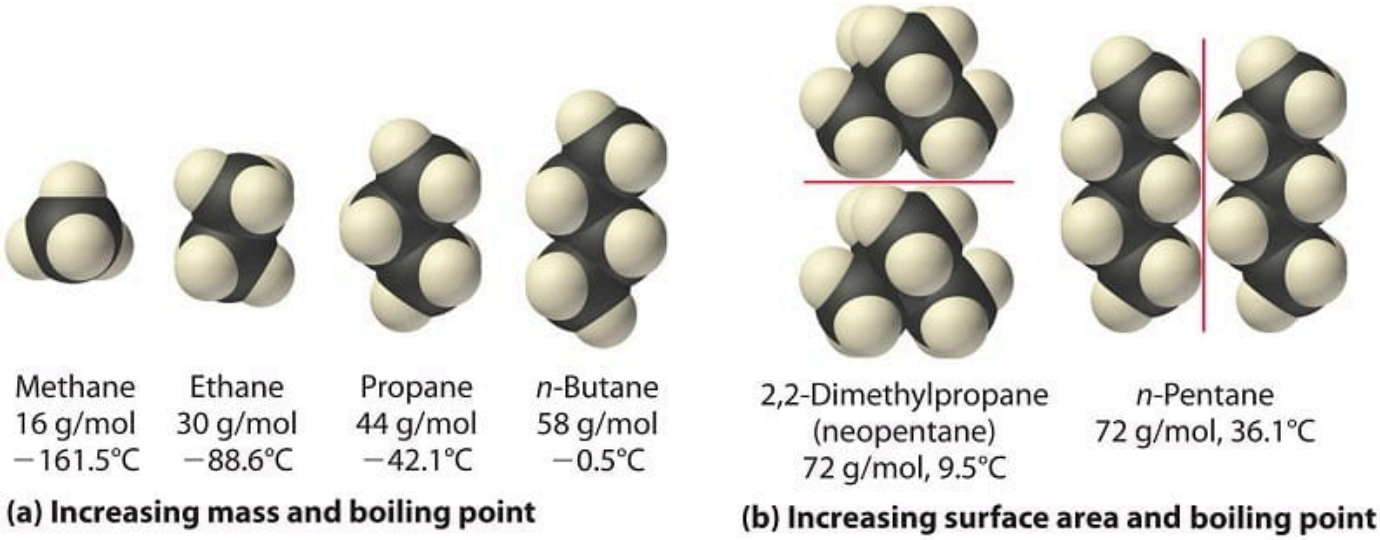


Figure 12.1.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger 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.

YouTube Video

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Video Discussing London/Dispersion Intermolecular Forces. Source: Dispersion Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 12.1.2

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 12.1.2

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 12.1.5. 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.

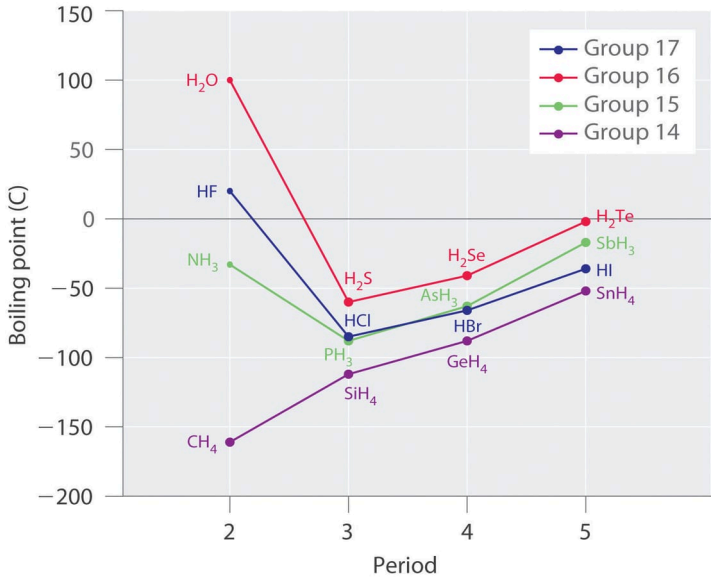


Figure 12.1.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously 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 12.1.6. 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.

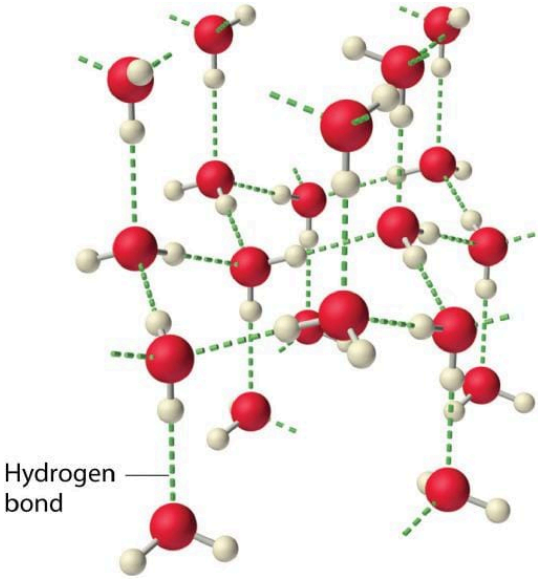


Figure 12.1.6: The Hydrogen-Bonded Structure of Ice

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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Video Discussing Hydrogen Bonding Intermolecular Forces. Source: Hydrogen Bonding Intermolecular Force, YouTube(opens in

new window) [youtu.be]

Example 12.1.3

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

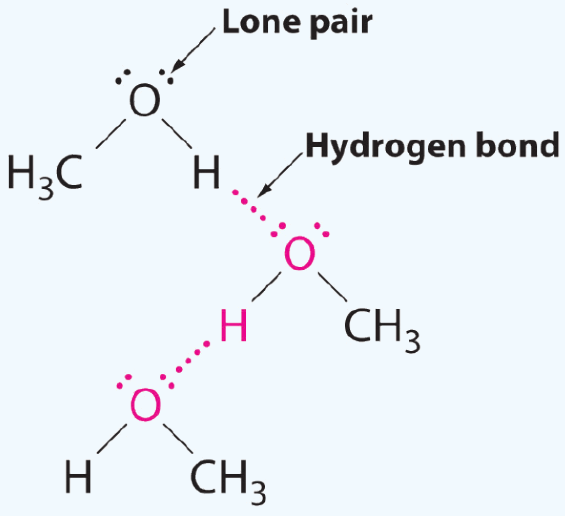
Strategy:

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 12.1.3

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 12.1.4: 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 12.1.4

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 12.1.5

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 12.1.6

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 12.1.1

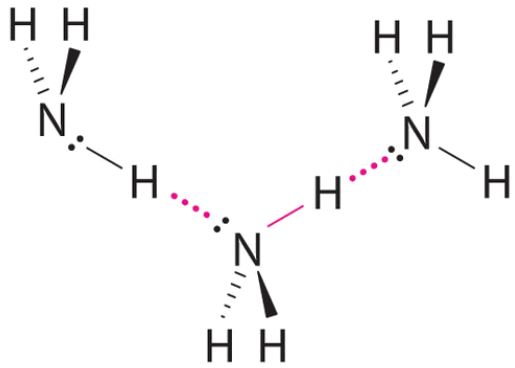
dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = –128°C)

Exercise 12.1.2

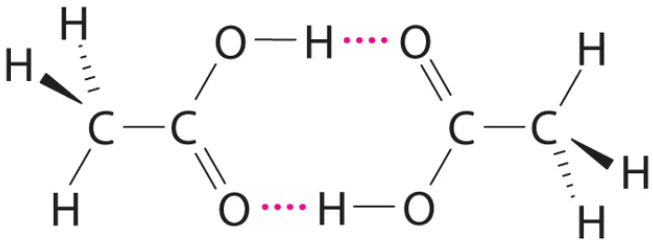
$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (–88.5°C) > SiH_4 (–111.8°C) > CH_4 (–161°C)

Exercise 12.1.3

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 12.1.4

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (–34.6°C) > Ne (–246°C)

Exercise 12.1.6

hydrogen bonding

dipole-dipole interactions

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12.2: Some Properties of Liquids

Learning Objectives

- To describe the unique properties of liquids.
- 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.

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:

1. surface tension,
2. capillary action, and
3. viscosity.

Surface Tension

If liquids tend to adopt the shapes of their containers, then, 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 (electrostatic) bonds has as surface tension that is 15-times lower: 4.6 x 10^{-1} J/m^2 (at 20°C).

Figure 12.2.1 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 (see the chapter opener photo). 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.

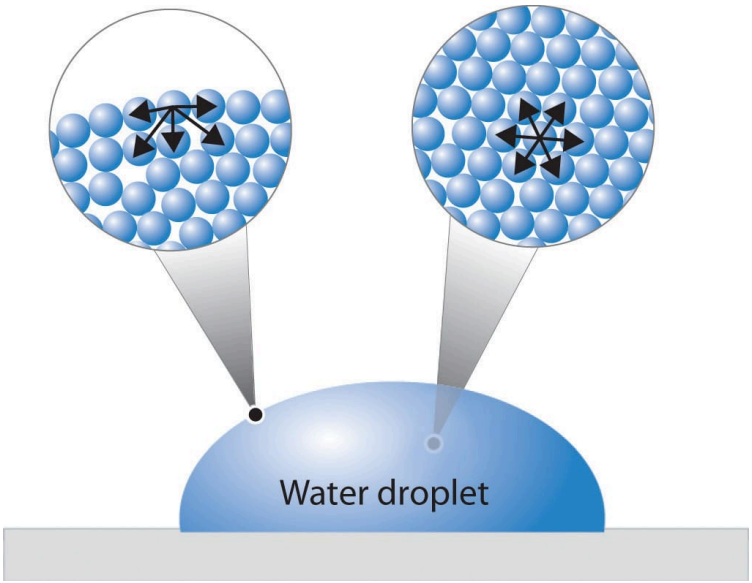


Figure 12.2.1: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.

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 better describe in the zero gravity condictions of space as Figure 12.2.2 indicates (and more so in the video link).



Figure 12.2.2: The Effects of the High Surface Tension of Liquid Water. The Full video can be found at https://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 12.2.1. 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 12.2.1: 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				
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.

YouTube Video

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Surface Tension, Viscosity, & Melting Point: https://youtu.be/OgKDGrdTRRM

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 12.2.3. When a glass capillary is put into a dish of water, water is drawn up into the tube. 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.

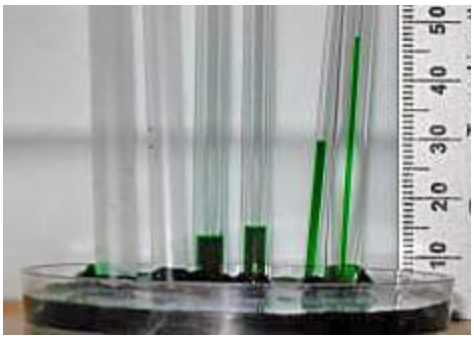


Figure 12.2.3: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.

When a glass capillary is placed in liquid water, water rises up into the capillary. The smaller the diameter of the capillary, the higher the water rises. The height of the water does *not* depend on the angle at which the capillary is tilted.

Note

- Cohesive forces bind molecules of the same type together
- Adhesive forces bind a substance to a surface

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

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 (part (a) in Figure 12.2.4). 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 (part (b) in Figure 12.2.4).

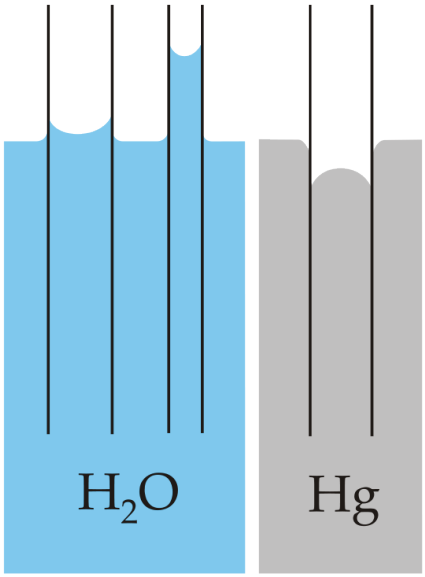


Figure used with permission from Wikipedia.

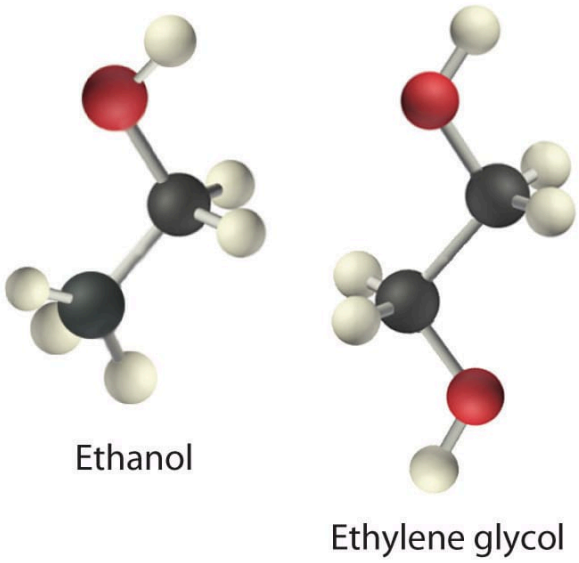
Note

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 12.2.1 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.

Note

Viscosity increases as intermolecular interactions or molecular size increases.

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.



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. 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 12.2.1

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 12.2.1

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: Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Vapor Pressure

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.

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

Vapor Pressure & Boiling Point: https://youtu.be/4QtcdpfRO1M

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 12.2.5), just as we did for a gas (Figure 10.19). 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.

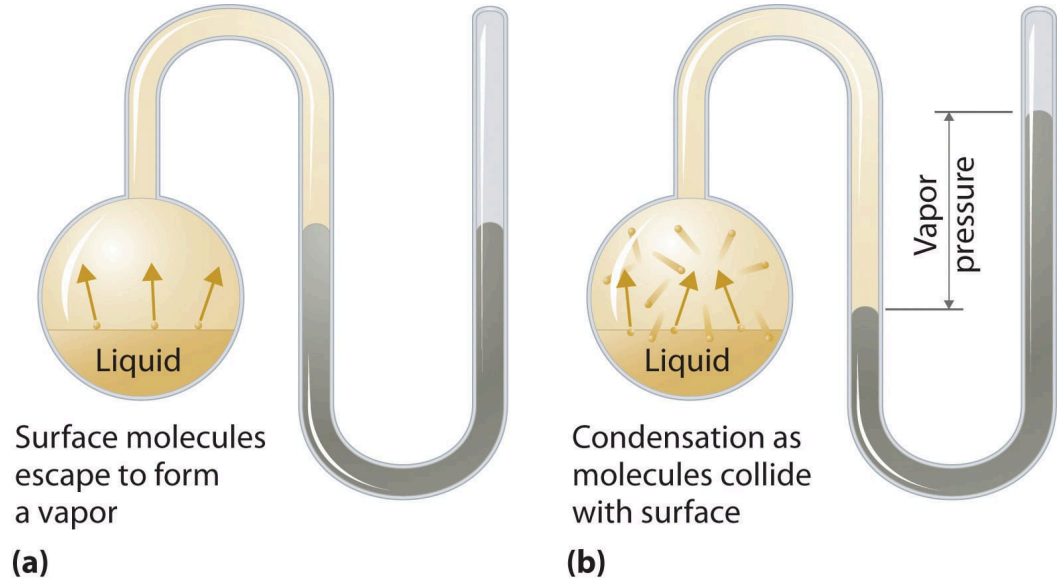


Figure 12.2.5: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 12.2.6. When a liquid is introduced into an evacuated chamber (part (a) in Figure 12.2.6), 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.

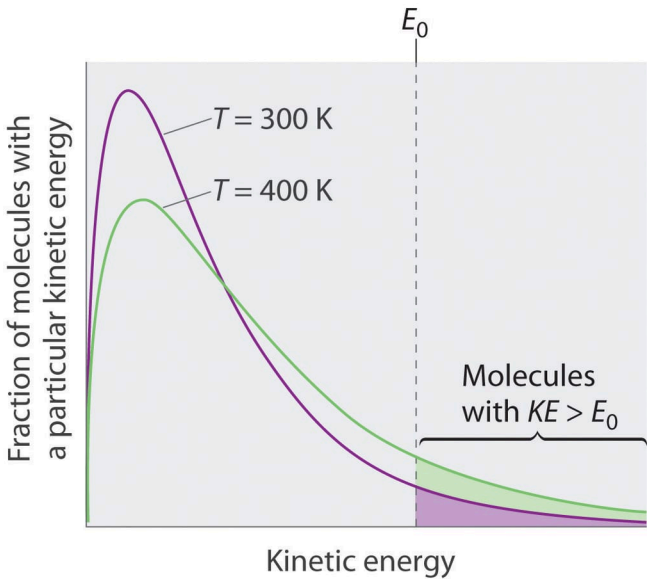


Figure 12.2.6: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant.

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 12.2.6). 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 12.2.7.

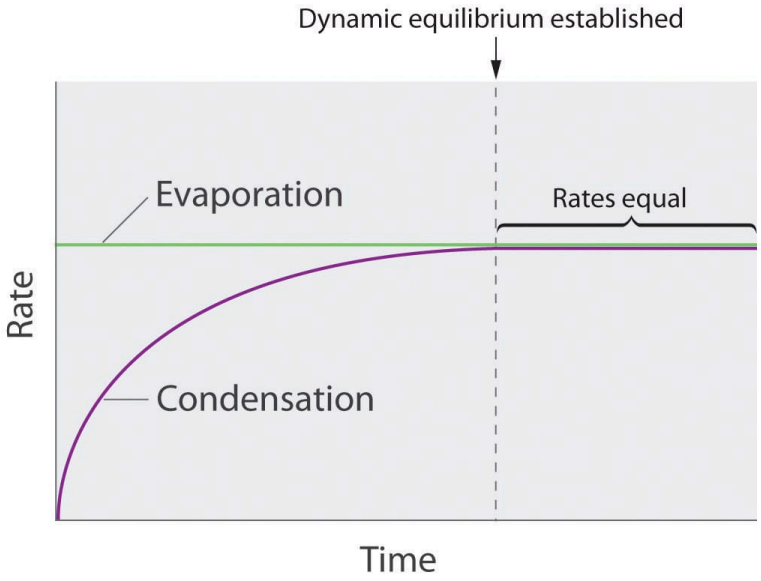


Figure 12.2.7: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation.

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 (Table 11.4) 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.

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 (Table 11.4). 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 12.2.8. 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.

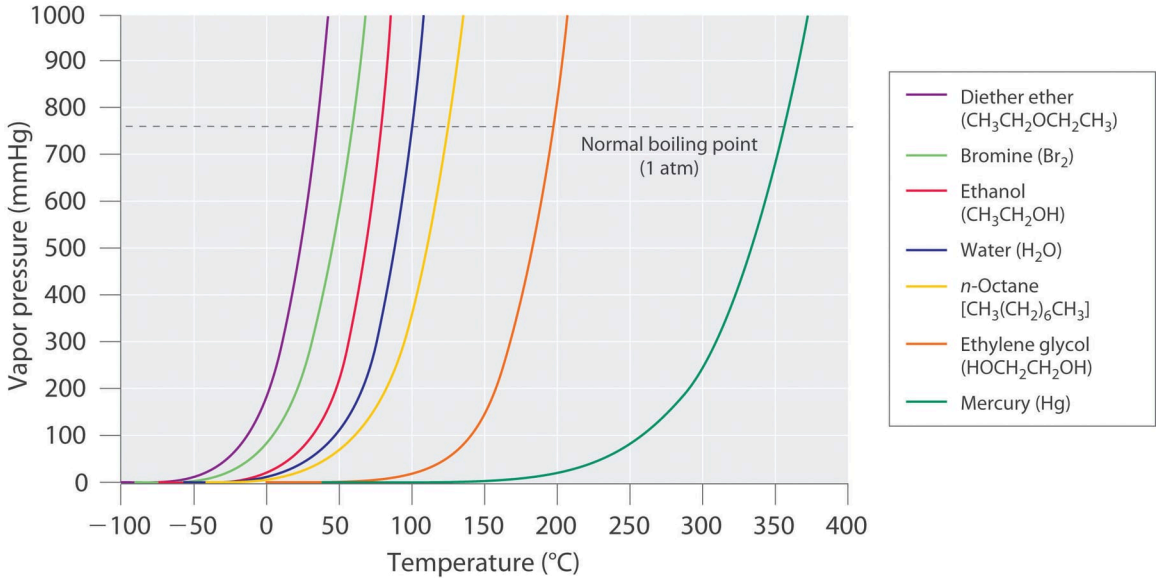


Figure 12.2.8: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the *P* = 1 atm line (dashed) is the normal boiling point of the liquid.

Note

Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.

The exponential rise in vapor pressure with increasing temperature in Figure 12.2.8 allows us to use natural logarithms to express the nonlinear relationship as a linear one.

$$\ln(P) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \tag{12.2.1}$$

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.

A plot of \ln P versus the inverse of the absolute temperature (1/T) is a straight line with a slope of $-\Delta H_{vap}/R$. Equation 12.2.1, 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 12.2.1, which is derived from the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{12.2.2}$$

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation 12.2.1 to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example 12.2.2.

Example 12.2.2: Vapor Pressure of Mercury

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

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 12.2.1 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 12.2.1 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 12.2.1 and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 12.2.1 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 kelvins because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 12.2.1 gives

$$\ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot K}\left(\frac{1}{(120+273)\ K} - \frac{1}{(80.0+273)\ K}\right) \tag{12.2.3}$$

$$\ln(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot \cancel{K}}\left(-2.88 \times 10^{-4}\ \cancel{K^{-1}}\right) \tag{12.2.4}$$

$$2.13 = -\Delta H_{vap}\left(-3.46 \times 10^{-4}\right) J^{-1} \cdot mol \tag{12.2.5}$$

$$\Delta H_{vap} = 61,400\ J/mol = 61.4\ kJ/mol \tag{12.2.6}$$

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):

$$\ln\left(\frac{P_2}{0.0888\ torr}\right) = \frac{-61,400\ \cancel{J/mol}}{8.314\ \cancel{J/mol}\ K^{-1}}\left(\frac{1}{(160+273)\ K} - \frac{1}{(80.0+273)\ K}\right) \tag{12.2.7}$$

Using the relationship $e^{\ln x} = x$, we have

$$\ln\left(\frac{P_2}{0.0888\ Torr}\right) = 3.86 \tag{12.2.8}$$

$$\frac{P_2}{0.0888\ Torr} = e^{3.86} = 47.5 \tag{12.2.9}$$

$$P_2 = 4.21 Torr \tag{12.2.10}$$

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 12.2.2: 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: 1896°C

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 12.2.8 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 12.2.2: 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
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 12.2.2 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.

Note

As pressure *increases*, the boiling point of a liquid *increases* and vice versa.

Example 12.2.3: Boiling Mercury

Use Figure 12.2.8 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

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Mercury boils at 356 °C at room pressure. To see video go to https://www.youtube.com/watch?v=0iizsbXWYoo

Given: data in Figure 12.2.8, 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 12.2.8 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 12.2.3: 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 12.2.8 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. 200°C

b. 450 mmHg

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.

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

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12.3: Some Properties of Solids

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 12.3.1.

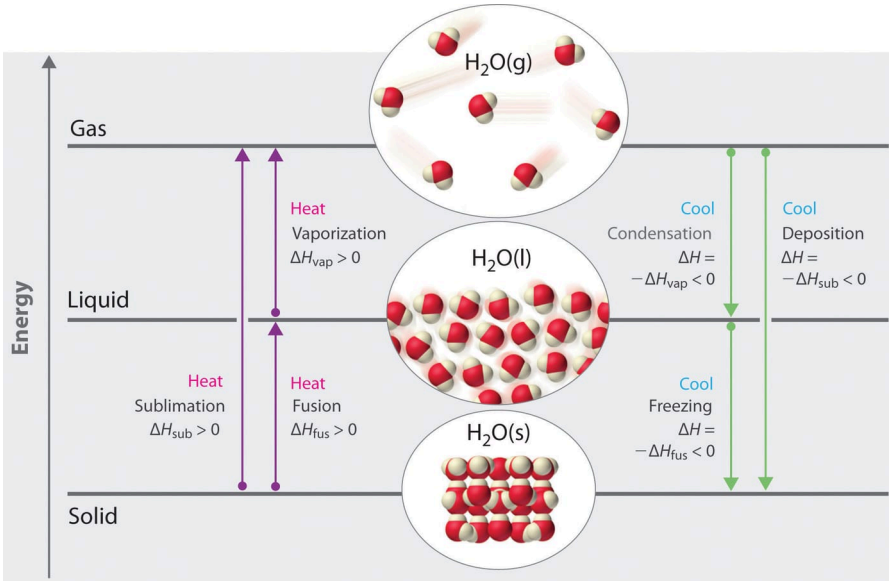


Figure 12.3.1: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows.

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 12.3.1.

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 12.3.1.

Table 12.3.1: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances

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

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
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).

> 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.

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 12.3.2); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure 12.3.1, 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.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{12.3.1}$$



Figure 12.3.2: 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 permisison from Wikipedia.

> Less energy is needed to allow molecules to move past each other than to separate them totally

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, as demonstrated later in Example 8.

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The Thermodynamics of Phase Changes: https://youtu.be/Uf2mAuP1BZY

Temperature Curves

The processes on the right side of Figure 12.3.1—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 12.3.3 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.

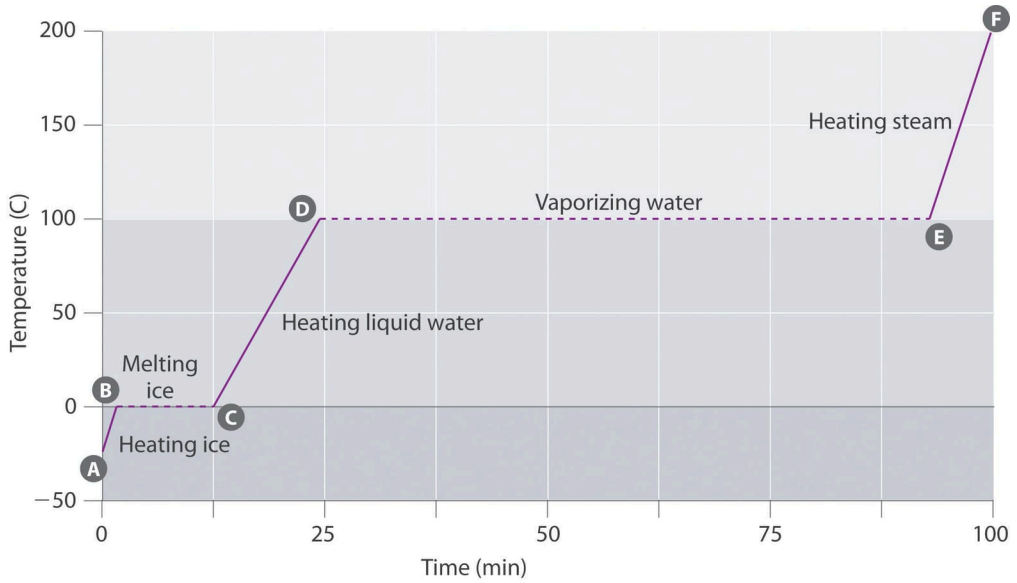


Figure 12.3.3: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and –23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

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 12.3.3, 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 12.3.3, 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 12.3.4 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 12.3.3, 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.

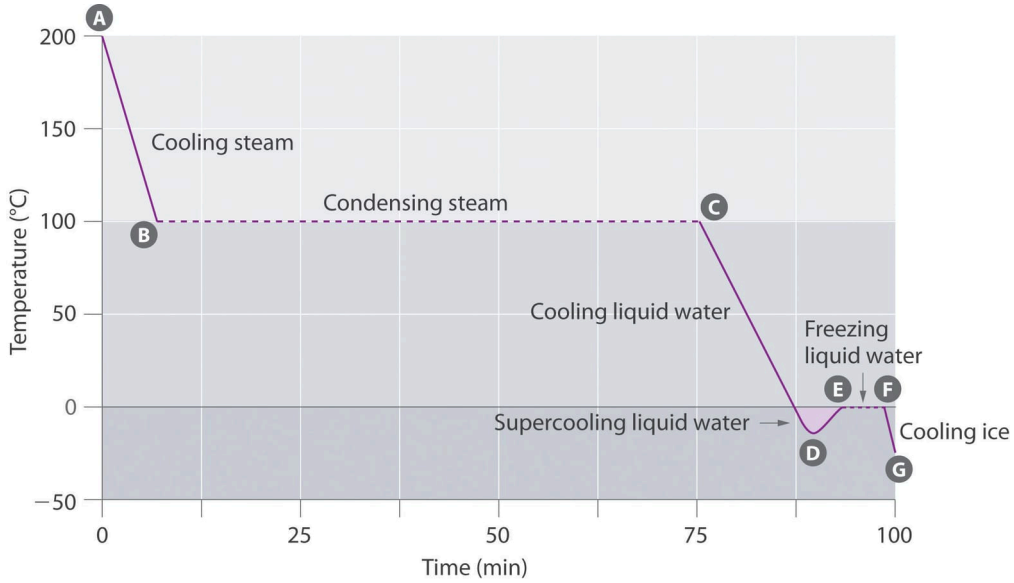


Figure 12.3.4: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid 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.

Example 12.3.1: Cooling Hot 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 values given into the general equation relating heat gained to heat lost (Equation 5.39) 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

$$q = mC_s\Delta T \tag{12.3.2}$$

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.

Exercise 12.3.1: 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 12.3.1

Answer: 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.

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.

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12.4: 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 12.4.1). 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 12.4.1) 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.

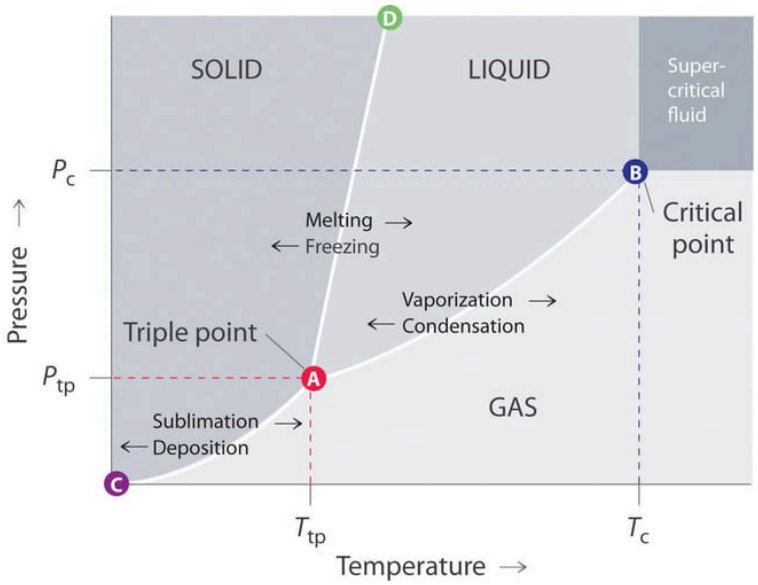


Figure 12.4.1: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

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 12.4.1, 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 12.4.1, 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 12.4.2 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).

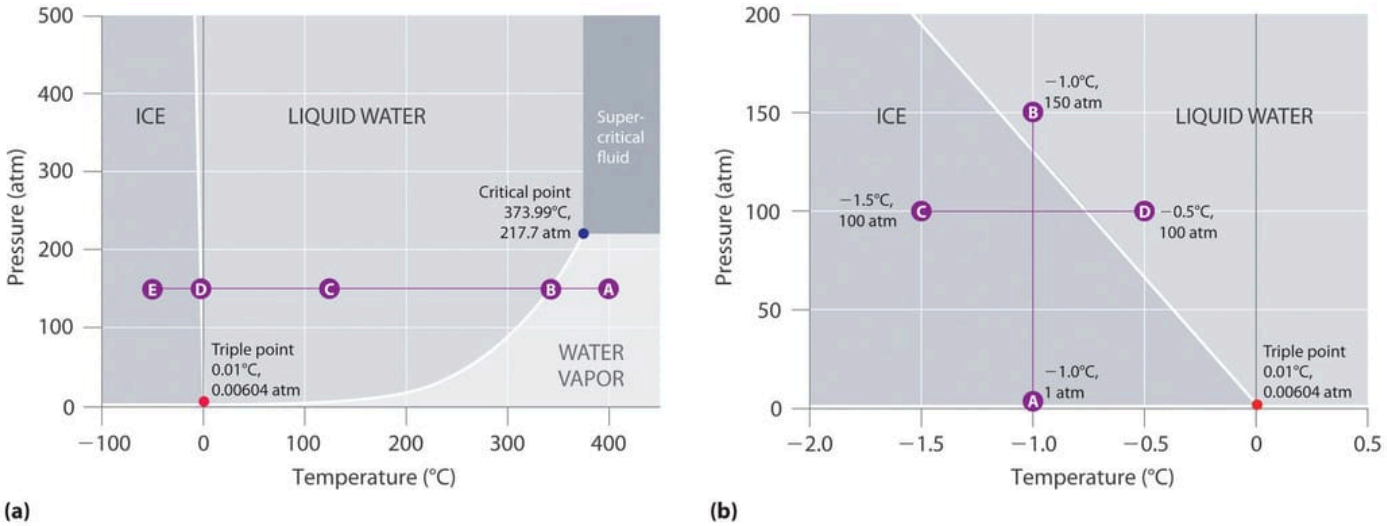


Figure 12.4.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 12.4.1).

The phase diagram for water illustrated in Figure 12.4.2*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 12.4.1; 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 12.4.2*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 12.4.1: Water

Referring to the phase diagram of water in Figure 12.4.2:

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 12.4.2. 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 12.4.2 . 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 12.4.2

Referring to the phase diagram of water in Figure 12.4.2, 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 12.4.3) 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.

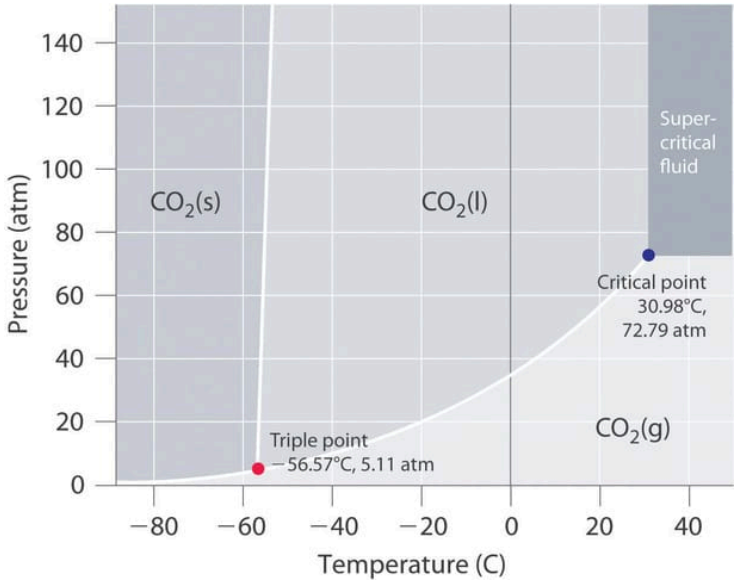


Figure 12.4.3: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

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 12.4.1.

Figure 12.4.1: 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.

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A Video Discussing Phase Diagrams. Video Source: Phase Diagrams(opens in new window) [youtu.be]

Answers

Exercise 12.4.2

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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12.5: Network Covalent Solids and Ionic 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 12.5.1: 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.

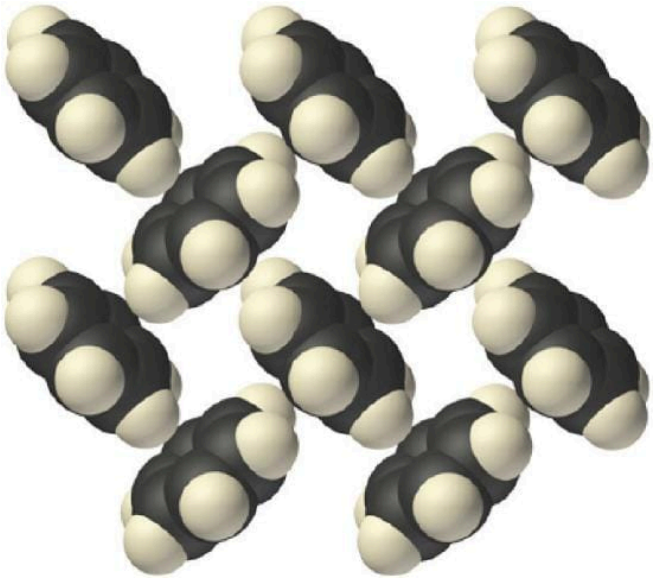
Ionic Solids

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

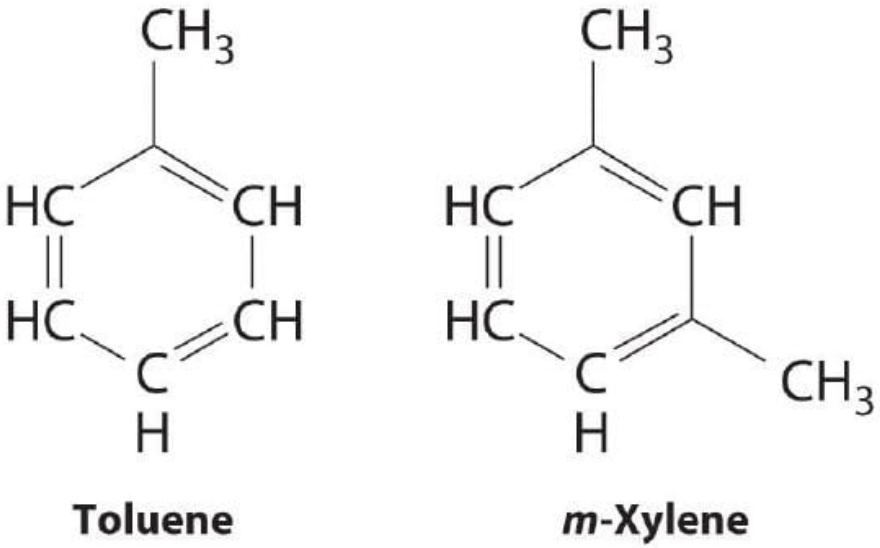
Molecular solids consist of atoms or molecules held to each other by dipole–dipole interactions, London dispersion forces, or hydrogen bonds, or any combination of these. The arrangement of the molecules in solid benzene is as follows:



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 12.5.1, 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.

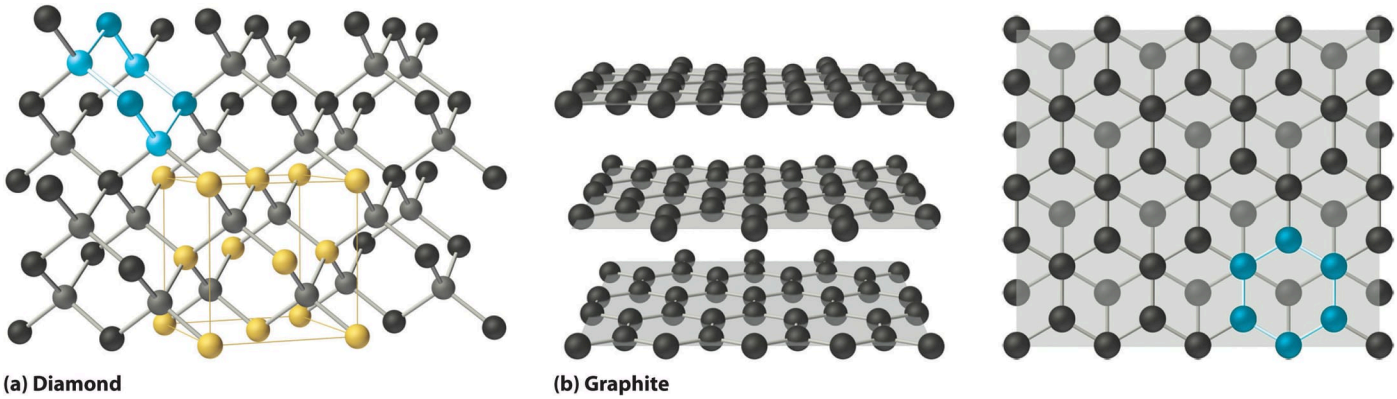


Figure 12.5.1: The Structures of Diamond and Graphite. (a) Diamond consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. This is easier to see in the rotating cube shown in Figure 12.5.2 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 12.5.1. 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 12.5.2 compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table 12.5.2: 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.

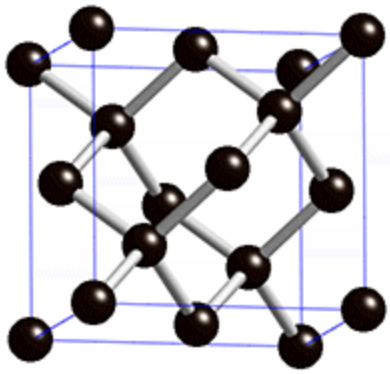


Figure 12.5.2: Rotating model of diamond cubic. (CC0; H.K.D.H. Bhadeshia via Wikipedia)

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 12.5.3 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.

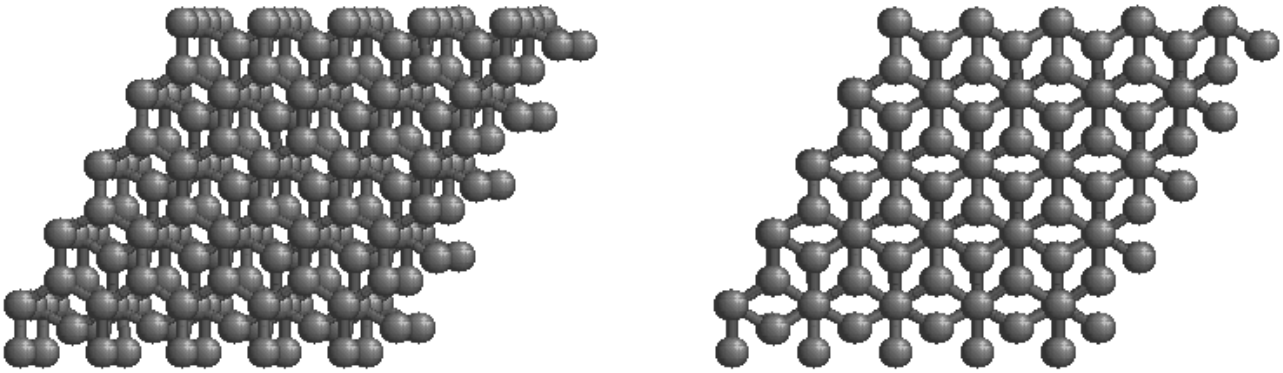


Figure 12.5.3: Animation of a rotating graphite structure. This is a stereogram and can be viewed in 3D if a viewer's eyes are crossed slightly to overlap the two panels. Images used with permission from Wikipedia.

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.

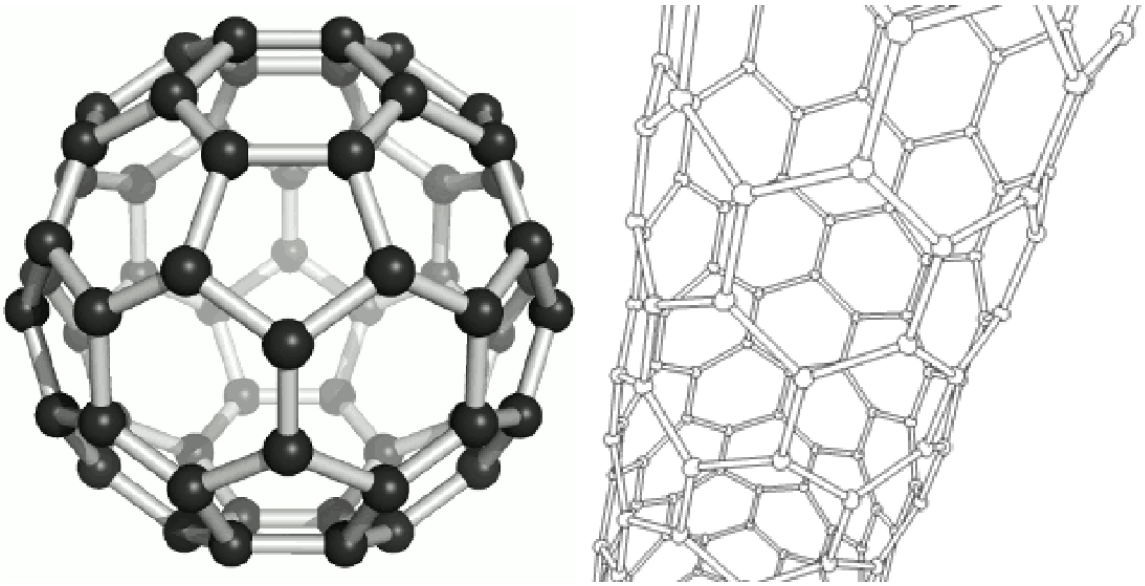


Figure 12.5.4: Example of fullerenes: a buckyball (C_{60} on left and an extended bucktube. Images used with permission from Wikipedia.

The C_{60} molecule (Figure 12.5.4; 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 12.5.4; 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 12.5.5. 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.

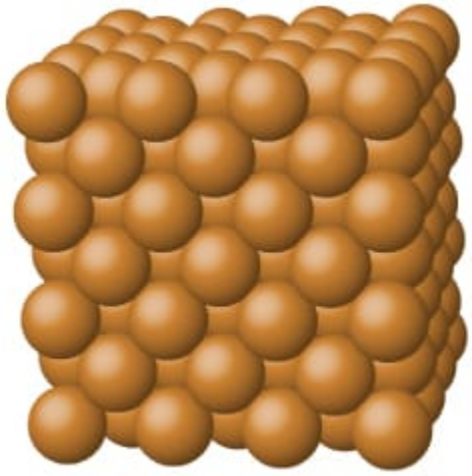


Figure 12.5.5: Copper is a metallic solid. (CC BY 4.0; OpenStax).

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.

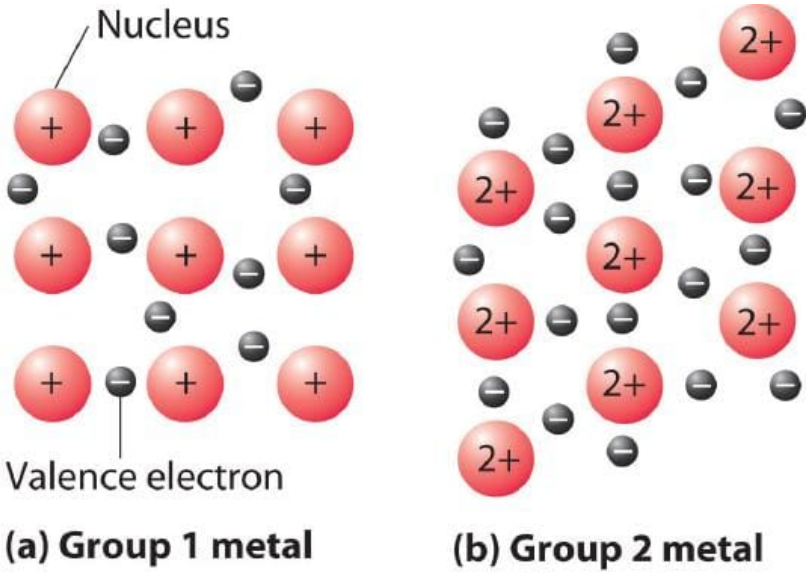


Figure 12.5.6: The Electron-Sea Model of Bonding in Metals. Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a "sea" of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting 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 12.5.6). 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 12.5.2.

Table 12.5.2: 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 12.5.1

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 12.5.1

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.

Contributors and Attributions

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Answers

Exercise 12.5.1

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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12.6: Crystal Structures

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 12.6.1: (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 12.6.2, 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.

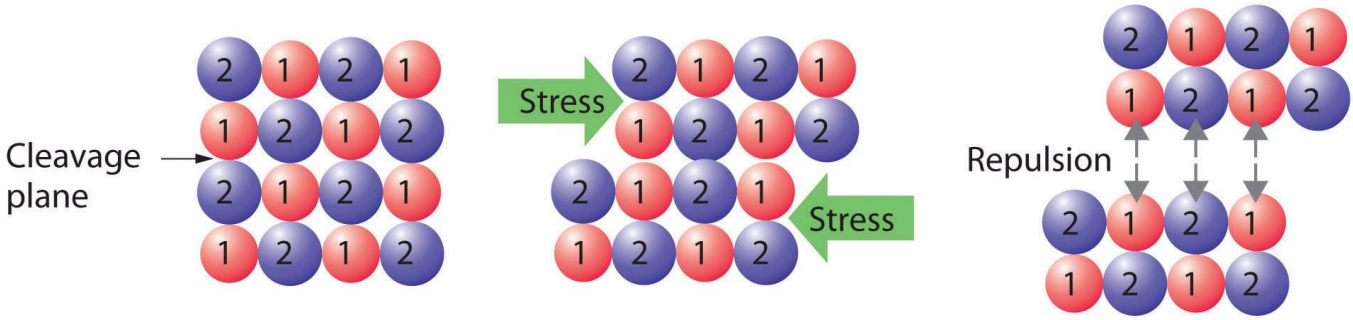


Figure 12.6.2: Cleaving a Crystal of an Ionic Compound along a Plane of Ions. Deformation of the ionic crystal causes one plane of atoms to slide along another. The resulting repulsive interactions between ions with like charges cause the layers to separate.

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.

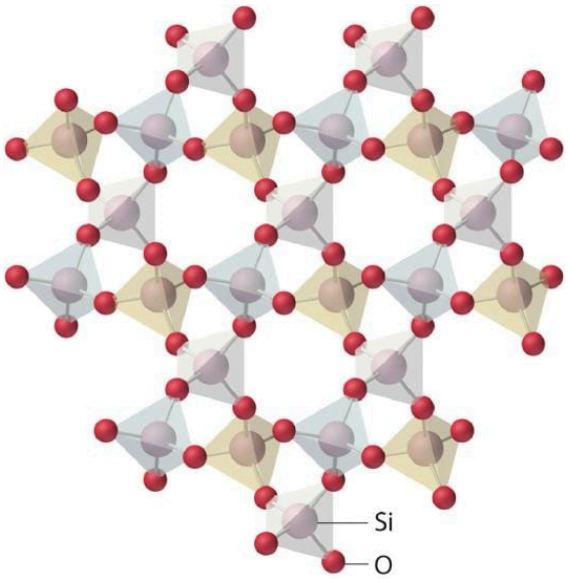


Figure 12.6.3: The lattice of crystalline quartz (SiO_2). The atoms form a regular arrangement in a structure that consists of linked tetrahedra.

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.

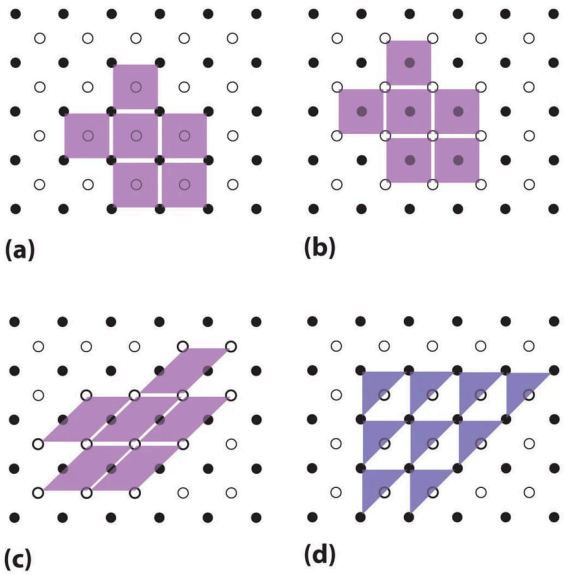


Figure 12.6.4: Unit Cells in Two Dimensions. (a–c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall 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 12.6.4. 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 12.6.4*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 12.6.5.

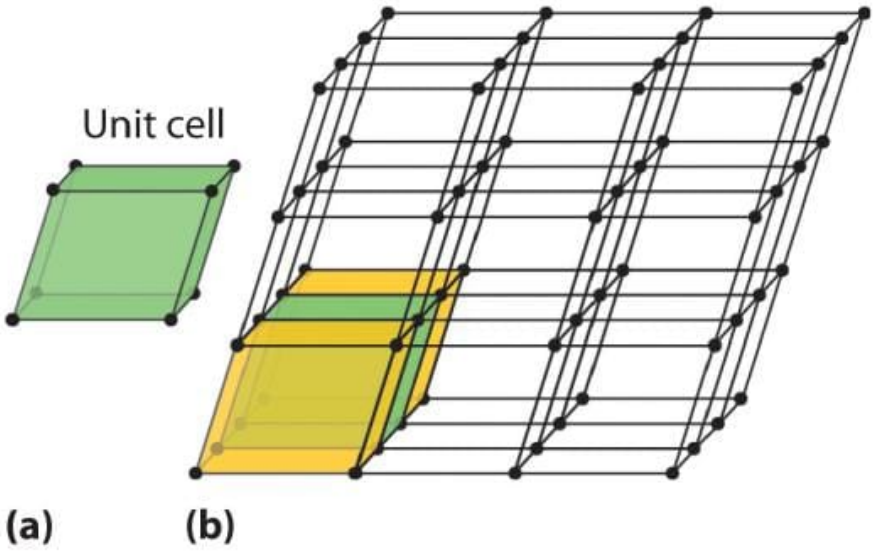


Figure 12.6.5: Unit Cells in Three Dimensions. These images show (a) a three-dimensional unit cell and (b) the resulting regular three-dimensional lattice.

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 12.6.6). 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.

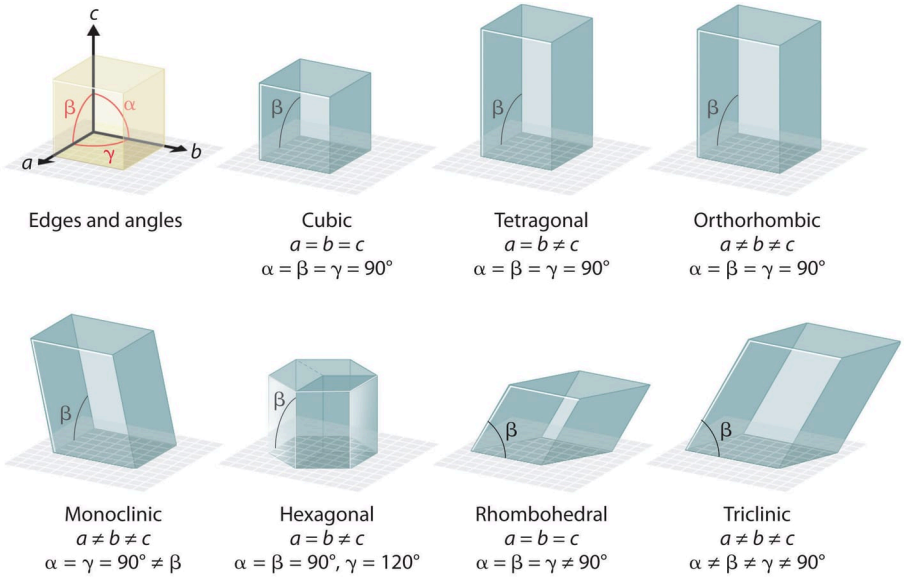


Figure 12.6.6: The General Features of the Seven Basic Unit Cells. The lengths of the edges of the unit cells are indicated by a, b, and c, and the angles are defined as follows: α, the angle between b and c; β, the angle between a and c; and γ, the angle between a and b.

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 12.6.7*a*). If the unit cell also contains an identical component in the center of the cube, then it is body-centered cubic (bcc) (12.6.7*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 12.6.7*c*).

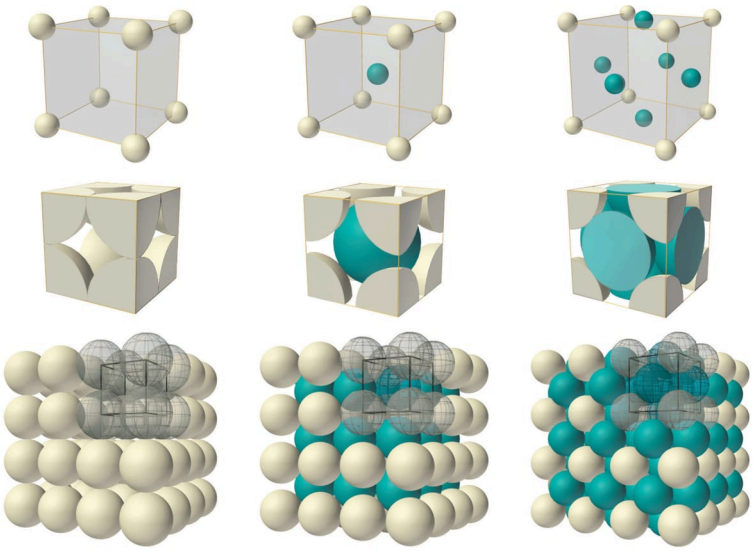


Figure 12.6.7: The Three Kinds of Cubic Unit Cell. For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that 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 12.6.7, 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 12.6.7. 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 12.6.7:), 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 12.6.1: The Unit Cell for Gold

Metallic gold has a face-centered cubic unit cell (12.6.7c). How many Au atoms are in each unit cell?

Given: unit cell

Asked for: number of atoms per unit cell

Strategy

Using Figure 12.6.7, 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 12.6.7, 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 12.6.1: Unit Cell for Iron

Metallic iron has a body-centered cubic unit cell (Figure 12.6.7*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 12.6.2: Density of Iron

Calculate the density of metallic iron, which has a body-centered cubic unit cell (Figure 12.6.7*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 12.6.1 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 12.6.2: Density of Gold

Calculate the density of gold, which has a face-centered cubic unit cell (Figure 12.6.7*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 $12.6.5a$. 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 $12.6.8$).

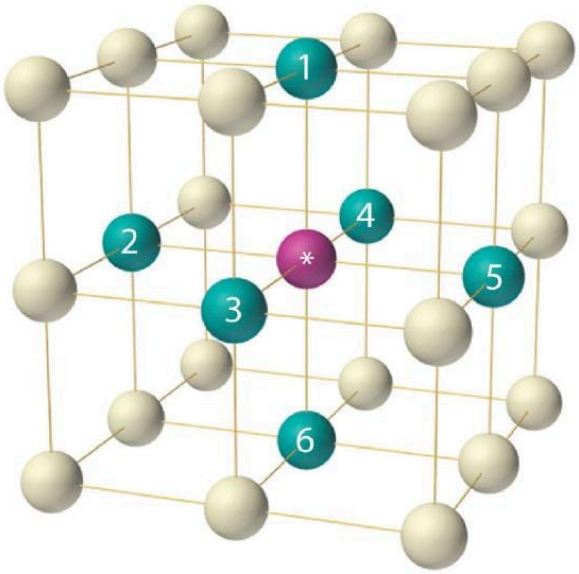


Figure $12.6.8$: The arrangement of atoms in a simple cubic unit cell. Each atom in the lattice has six nearest neighbors in an octahedral arrangement.

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 $12.6.8$, 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 $12.6.6a$. 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 12.6.9*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.

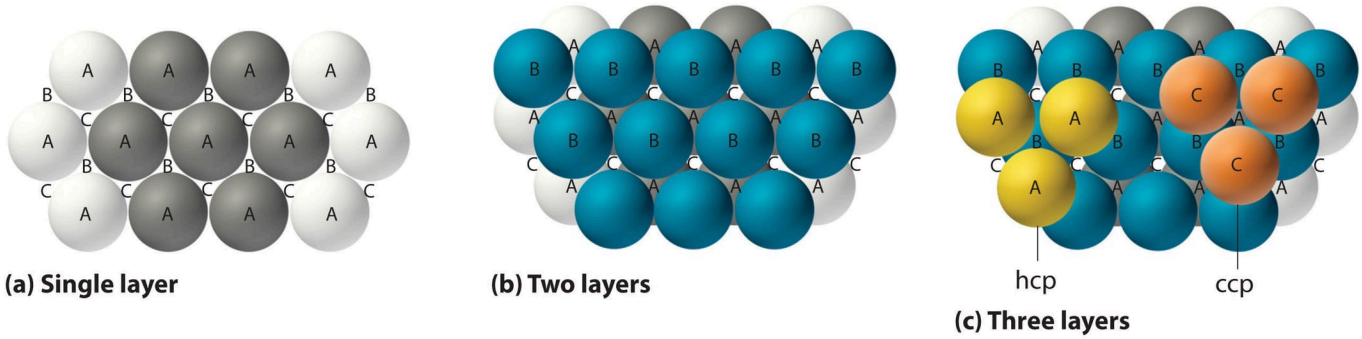


Figure 12.6.9: Close-Packed Layers of Spheres. (a) In this single layer of close-packed spheres, each sphere is surrounded by six others in a hexagonal arrangement. (b) Placing an atom at a B position prohibits placing an atom at any of the adjacent C positions and results in all the atoms in the second 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 12.6.9*a*, we obtain the two-layered structure shown in Figure 12.6.9*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 12.6.9*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 12.6.9*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 12.6.9*b*). Because the ccp structure contains hexagonally packed layers, it does not look particularly cubic. As shown in Figure 12.6.9*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).

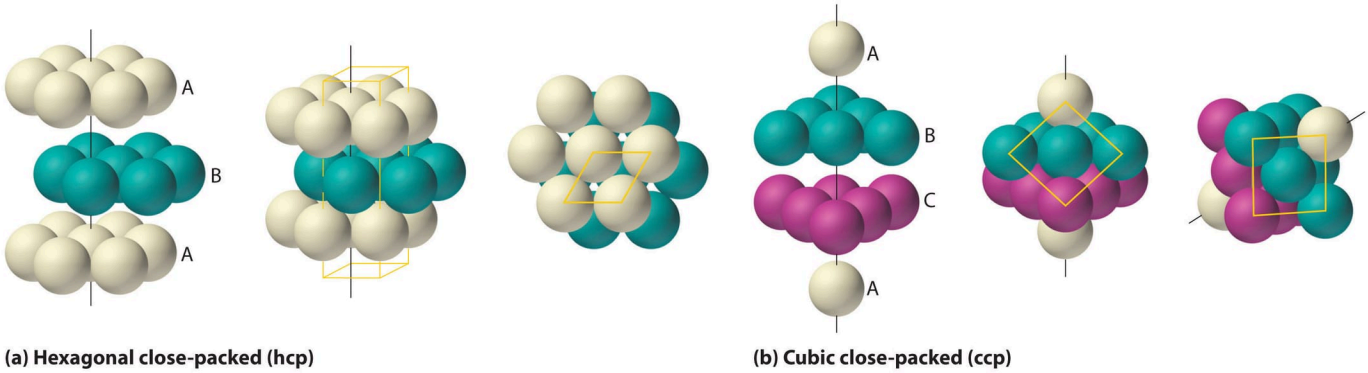


Figure 12.6.10. The ccp structure in (b) is shown in an exploded view, a side view, and a rotated view. The rotated view emphasizes the fcc nature of the unit cell (outlined). The line that connects the atoms in the first and fourth layers of the ccp structure is the body diagonal of the cube.

Table 12.6.1 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 12.6.1: 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 12.6.1**: Unit Cell for Iron**

two

Exercise 12.6.2**: Density of Gold**

19.29 g/cm^3

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12.7: Energy Changes in the Formation of Ionic Crystals

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13: SOLUTIONS AND THEIR PHYSICAL PROPERTIES

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

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13.1: Types of Solutions - Some Terminology

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)

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:

$$\mathrm{Zn(NO_3)_2\,(s) + H_2O\,(l)\ \rightarrow Zn^{2+}\,(aq) + 2\,NO_3^-\,(aq)}$$

Because $\mathrm{Zn(NO_3)_2}$ 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:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq)\ \rightarrow Zn^{2+}\,(aq) + 2\,Cl^-\,(aq) + H_2\,(g)}$$

> *Dissolution of a solute in a solvent to form a solution typically does not involve a chemical transformation and largely consist of breaking intermolecular forces rather than covalent bonds.*

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.

Mercury Amalgams: Examples of solid Solutions

An amalgam is an alloy of mercury with another metal. It may be a liquid, a soft paste or a solid, depending upon the proportion of mercury. These alloys are formed through metallic bonding, with the electrostatic attractive force of the conduction electrons working to bind all the positively charged metal ions together into a crystal lattice structure. Almost

all metals can form amalgams with mercury including aluminum (Video 13.1.1), the notable exceptions being iron, platinum, tungsten, and tantalum. Silver-mercury amalgams are important in dentistry, and gold-mercury amalgam is used in the extraction of gold from ore.

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 13.1.1: Aluminum dissolving into Mercury.

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.

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13.2: Solution 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 13.2.1 reviews the methods for calculating the molarity and mole fraction of a solution when the masses of its components are known.

Example 13.2.1: 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 13.2.1: 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:

$$\text{molality (m)} = \frac{\text{moles solute}}{\text{kilogram solvent}} \tag{13.2.1}$$

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):

$$\text{mass percentage} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \tag{13.2.2}$$

$$\text{parts per million (ppm)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \tag{13.2.3}$$

$$\text{parts per billion (ppb)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \tag{13.2.4}$$

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 13.2.2: 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 13.2.2: 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 13.2.1 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 13.2.3.

*Table 13.2.1: 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 13.2.3: 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 13.2.3: 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 13.2.1: Molarity and Mole Fraction

6.10 M HCl

$\chi_{HCl} = 0.111$

Exercise 13.2.2: Molarity of Lead Solution

4.3×10^{-8} M

2×10^{-6} g

Exercise 13.2.3: Toluene/Benzene Solution

mass percentage toluene = 24.8%

$\chi_{toluene} = 0.219$

2.35 M toluene

3.59 m toluene

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13.3: Intermolecular Forces and the Solution Process

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.

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.

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 $13.3.1$. The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{13.3.1}$$

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.

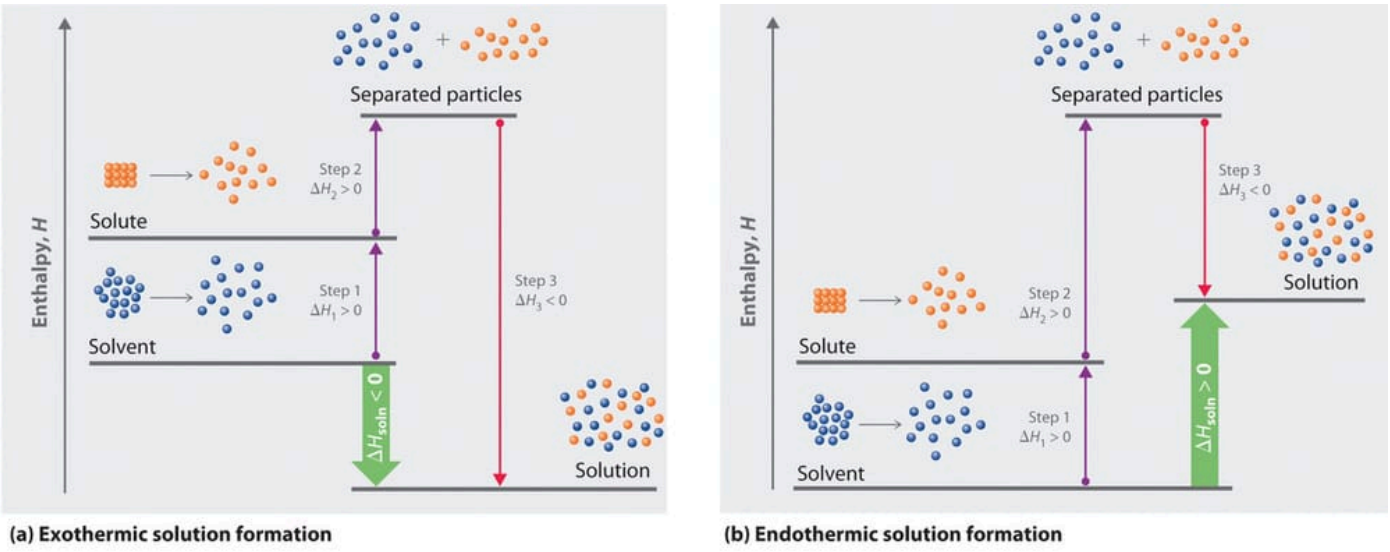


Figure 13.3.1: Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation 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 13.3.2).



Figure 13.3.2: 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.

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. 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 $13.3.1$. 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 $13.3.1$: 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
O_2	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 $13.3.3$), the region between the two layers. 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).



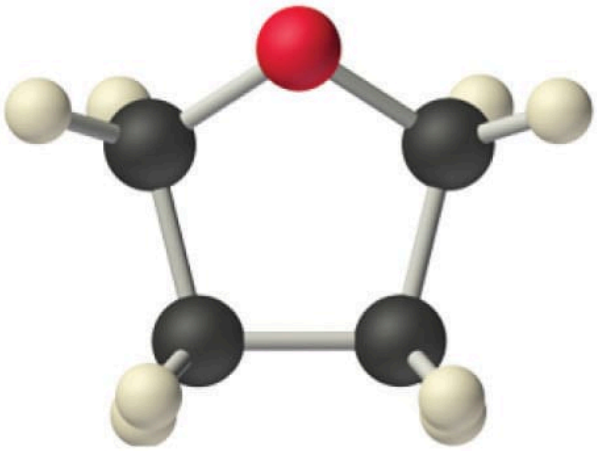
Figure 13.3.3: Immiscible Liquids. Separatory funnel demonstrating the separation of oil and colored water. from Wikipedia

The solubilities of simple alcohols in water are given in Table 13.3.2.

Table 13.3.2: Solubilities of Straight-Chain Organic Alcohols in Water at 20°C

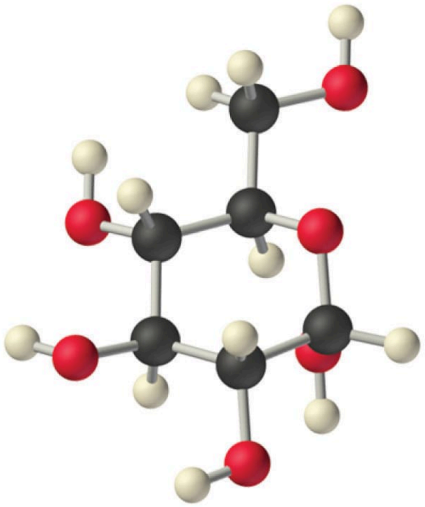
Alcohol	Solubility (mol/100 g of H_2O)
methanol	completely miscible
ethanol	completely miscible
n-propanol	completely miscible
n-butanol	0.11
n-pentanol	0.030
n-hexanol	0.0058
n-heptanol	0.0008

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.



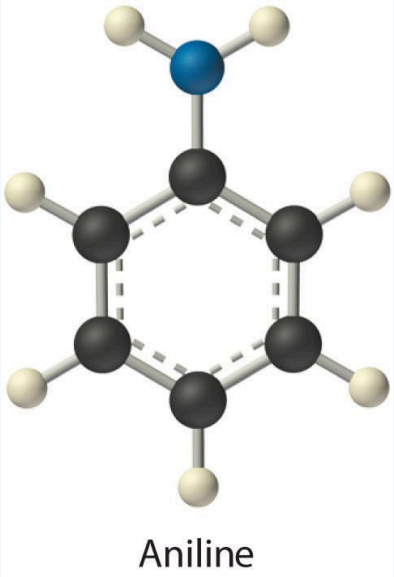
D-Glucose

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 13.3.1

Identify the most important solute–solvent interactions in each solution.

a. iodine in benzene
b. aniline ($C_6H_5NH_2$) in dichloromethane (CH_2Cl_2)



c. iodine in water

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 $I2$ are both nonpolar molecules. The only possible attractive forces are London dispersion forces.
b. Aniline is a polar molecule with an $-\mathrm{NH_2}$ group, which can act as a hydrogen bond donor. Dichloromethane is also polar, but it has no obvious hydrogen bond acceptor. Therefore, the most important interactions between aniline and CH_2Cl_2 are likely to be London 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 I_2 in water ($1.3 \times 10^{-3}\ mol/L$ at 25°C) is due to London dispersion forces.

Exercise 13.3.1

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

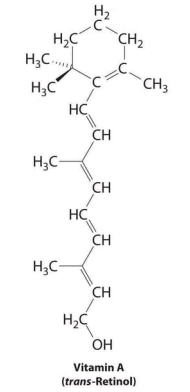
Answer:

a. hydrogen bonding
b. London interactions
c. London dispersion forces

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.

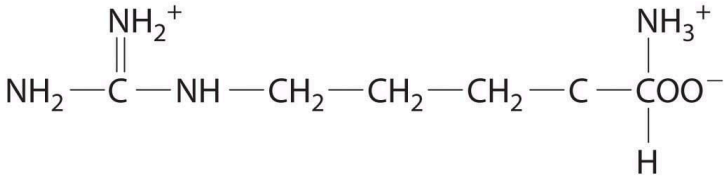
The difference between hydrophilic and hydrophobic substances has substantial consequences in biological systems. For example, vitamins can be classified as either fat soluble or water soluble. Fat-soluble vitamins, such as vitamin A, are mostly nonpolar, hydrophobic molecules. As a result, they tend 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.



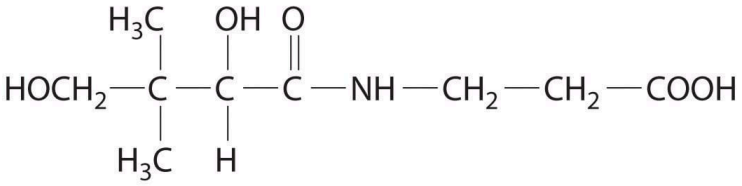
Because water-soluble vitamins are rapidly excreted, the risk of consuming them in excess is relatively small. Eating a dozen oranges a day is likely to make you tired of oranges long before you suffer any ill effects due to their high vitamin C content. In contrast, fat-soluble vitamins constitute a 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 13.3.2

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:

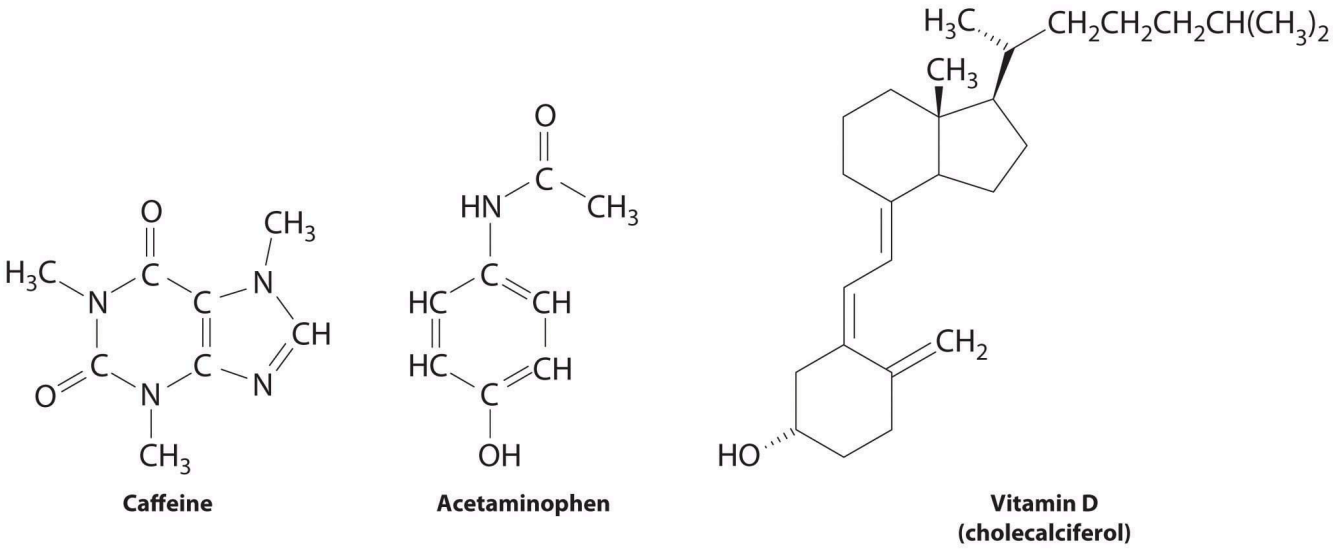
Based on the structure of each compound, decide whether it is hydrophilic or hydrophobic. If it is hydrophilic, it is likely to be required on a daily basis.

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 13.3.2

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: Caffeine and acetaminophen are water soluble and rapidly excreted, whereas vitamin D is fat soluble and slowly excreted

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 $ceSiO_2$ 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, 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

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.

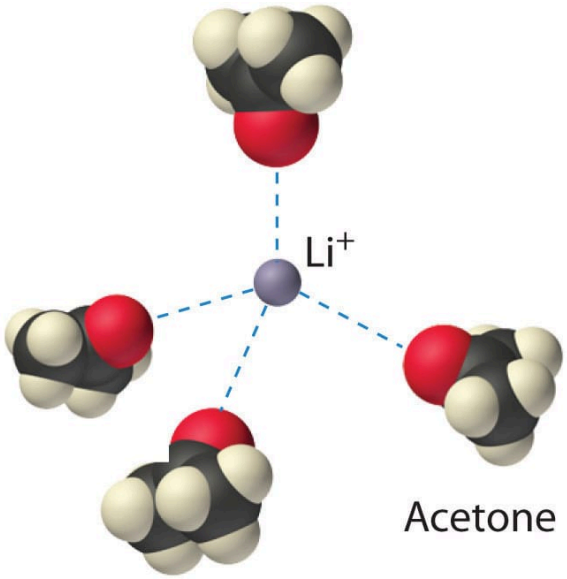


Figure 13.3.4: Ion–Dipole Interactions in the Solvation of Li+ Ions by Acetone, a Polar Solvent

The interaction of water with Na+ and Cl– ions in an aqueous solution of NaCl was illustrated in Figure 4.3. The ion–dipole interactions between Li+ ions and acetone molecules in a solution of LiCl in acetone are shown in Figure 13.3.4. The energetically favorable Li+–acetone interactions make ΔH_3 in Figure 13.1 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 Li+ and 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.

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. 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.

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13.4: Solution Formation and Equilibrium

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,

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 (part (a) in Figure 13.4.1). 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:

$$\text{solute} + \text{solvent} \underset{\text{dissolution}}{\overset{\text{crystallization}}{\rightleftharpoons}} \text{solution} \tag{13.4.1}$$

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.

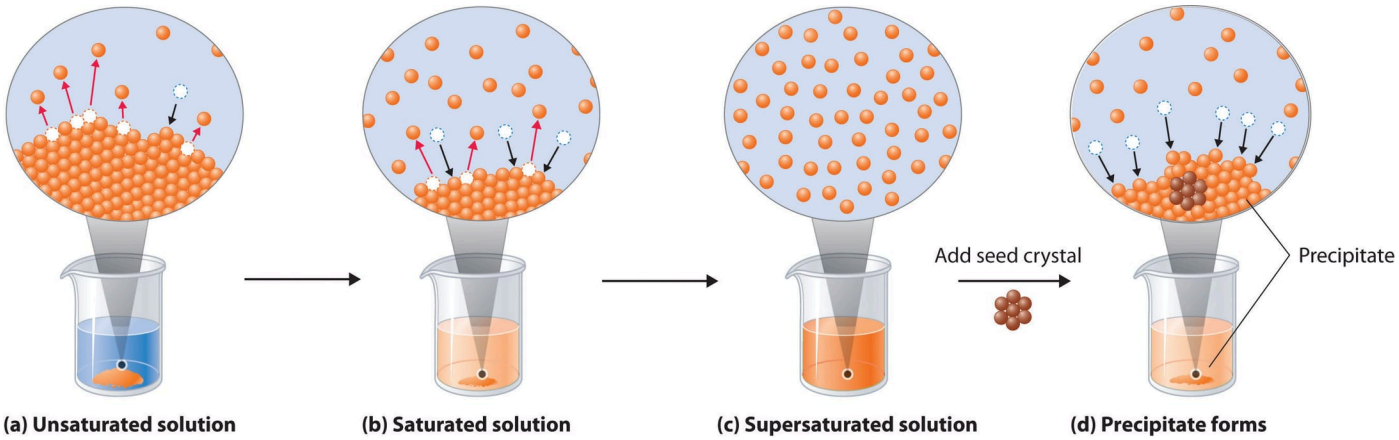


Figure 13.4.1 Dissolution and Precipitation. (a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the 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. (CC BY-SA-NC 3.0; anonymous)

Solubility as a Function of Temperature

Figure 13.4.2 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 CH_3CO_2Na) exhibit a dramatic increase in solubility with increasing temperature. Others (such as $NaCl$ and K_2SO_4) exhibit little variation, and still others (such as Li_2SO_4) become less soluble with increasing temperature.

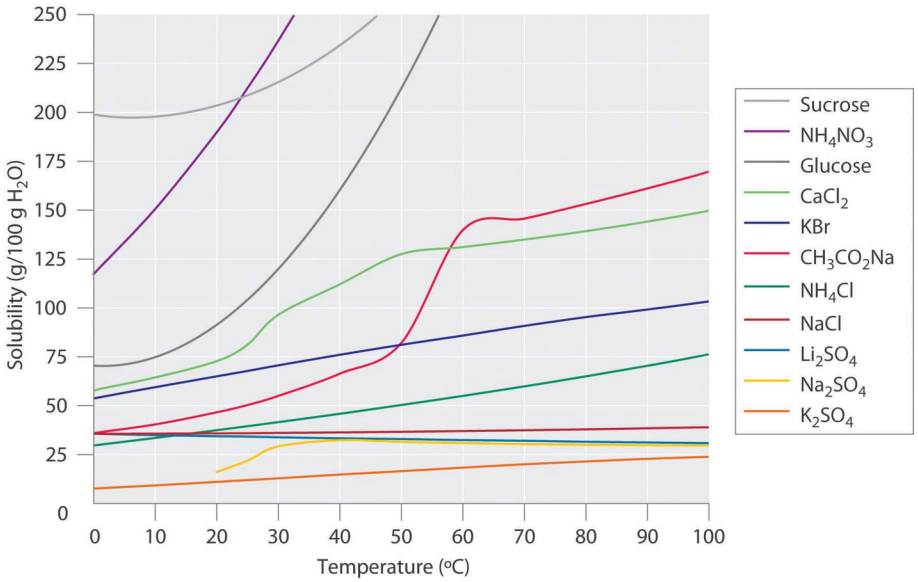


Figure 13.4.2: Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds. (CC BY-SA-NC 3.0; anonymous)

Notice in particular the curves for NH_4NO_3 and $CaCl_2$. 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 13.4.2 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.

Fractional Crystallization

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 (Figure 13.4.3). 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 13.4.2, 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.

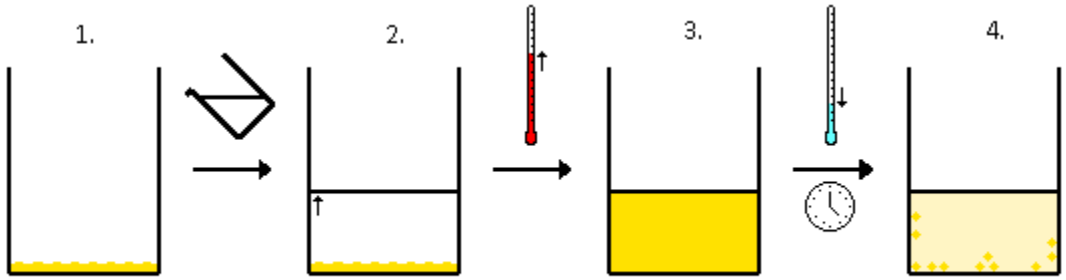


Figure 13.4.3: Steps in a Fractional crystallization technique: (1 to 2) Solvent added (clear) to compound (orange) (2 to 3) Solvent heated to give saturated compound solution (orange) (3 to 4) Saturated compound solution (orange) allowed to cool over time to give crystals (orange) and a saturated solution (pale-orange). (Public Domain; Quantockgoblin via Wikipedia)

Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure 13.4.2 and from

antibiotics to enzymes to drugs (Figure 13.4.4). 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.



Figure 13.4.4: Image of a single solvent, slowly cooling ibuprofen salt crystallizing. (CC BY-SA 2.5 Generic; Jacopo Werther via Wikipedia).

Summary

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 most substances depends strongly on the temperature. 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.

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13.5: Solubilities of Gases

The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14}, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure 13.5.1). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

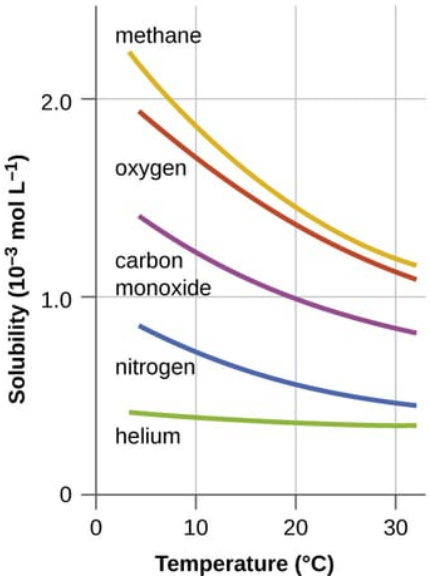


Figure 13.5.1: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure 13.5.2).



Figure 13.5.2: (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure 13.5.3). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."

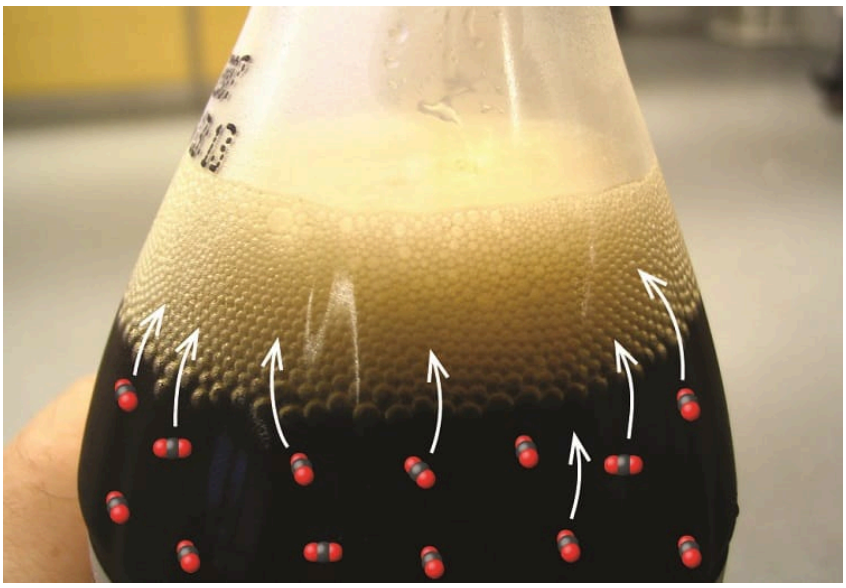


Figure 13.5.3: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

For many gaseous solutes, the relation between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_g = kP_g \tag{13.5.1}$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry's law: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

Example 13.5.1: Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is 1.38×10^{-3} mol L^{-1}. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g, of a gas (1.38×10^{-3} mol L^{-1}, in this case) is directly proportional to the pressure, P_g, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both C_g and P_g, we can rearrange this expression to solve for k.

$$\begin{aligned} C_g &= kP_g \\ k &= \frac{C_g}{P_g} \\ &= \frac{1.38 \times 10^{-3}\ \text{mol L}^{-1}}{101.3\ \text{kPa}} \\ &= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \\ &\quad (1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1}) \end{aligned}$$

Now we can use k to find the solubility at the lower pressure.

$$C_g = kP_g \tag{13.5.2}$$

$$\begin{aligned} &1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa} \\ &(\text{or } 1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1} \times 155\ \text{torr}) \\ &= 2.82 \times 10^{-4}\ \text{mol L}^{-1} \end{aligned} \tag{13.5.3}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Exercise 13.5.1

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Answer available at the end of this section.

Case Study: Decompression Sickness ("The Bends")

Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

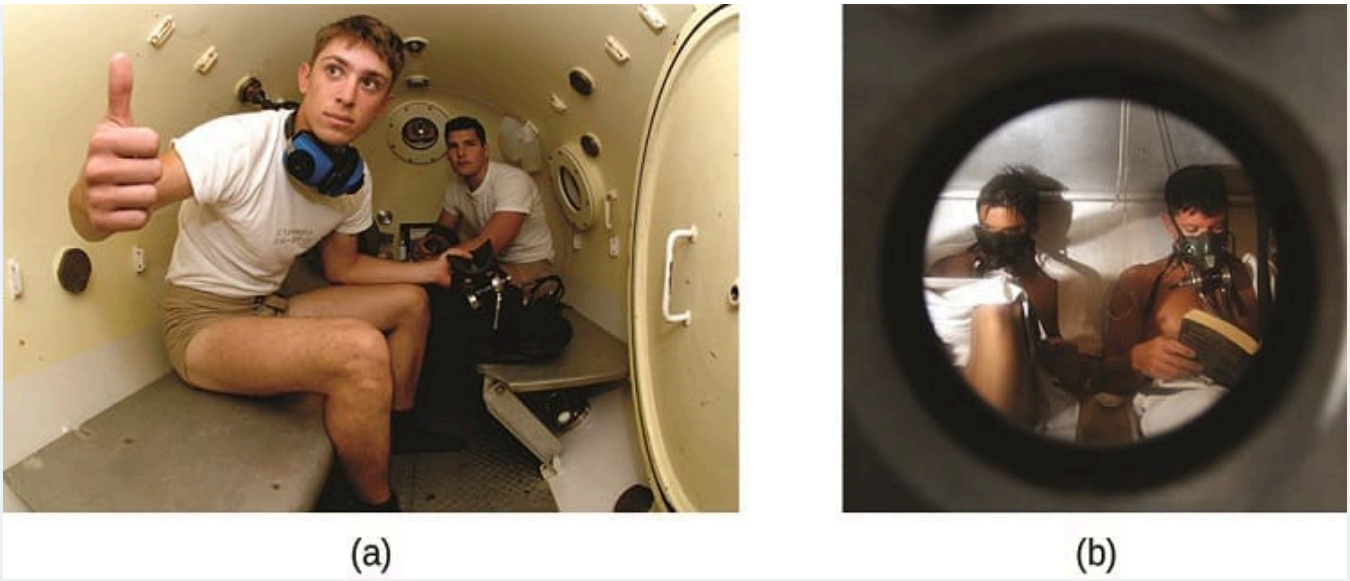
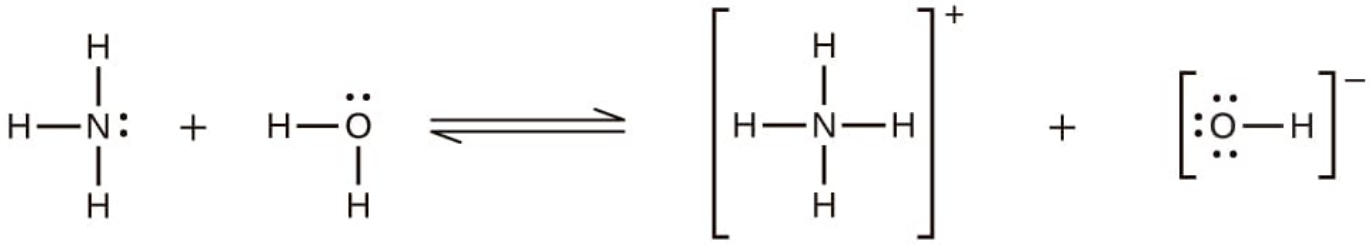


Figure 13.5.4: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 13.5.4).

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos (Figure 13.5.5), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO_2 were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.



(a) (b)

Figure 13.5.5: (a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)

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

Henry's Law (The Solubility of Gases in Solvents): https://youtu.be/fiJZCGpArJI

Answers

Exercise 13.5.1

7.25×10^{-3} g in 100.0 mL or 0.0725 g/L

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13.6: Vapor Pressures of Solutions

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.

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 13.6.1, 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.

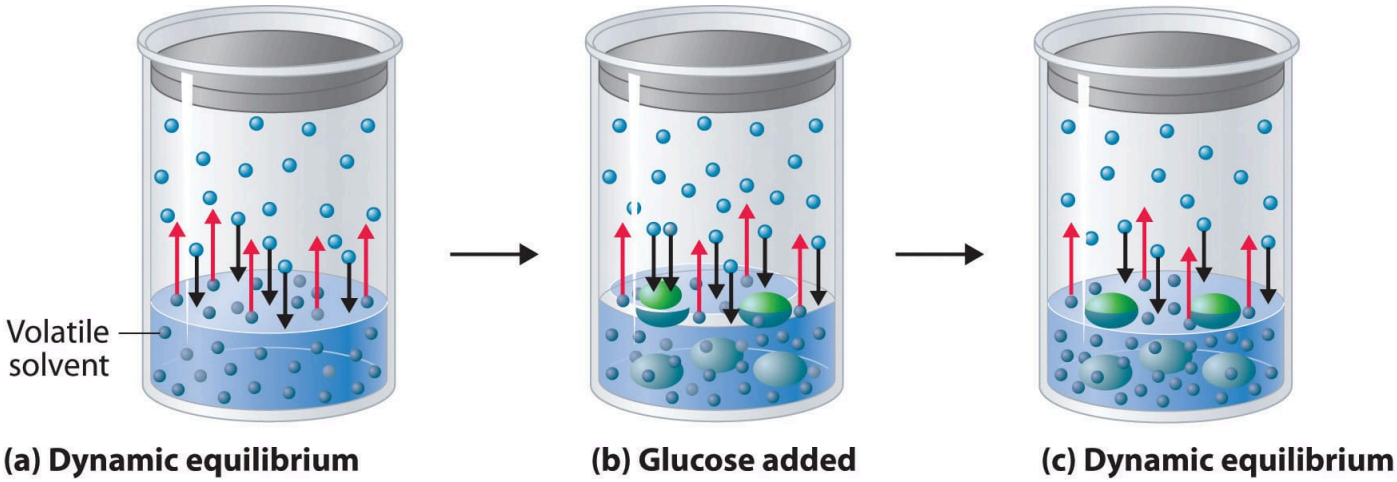


Figure 13.6.1: A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water. (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile 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 13.6.2 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.

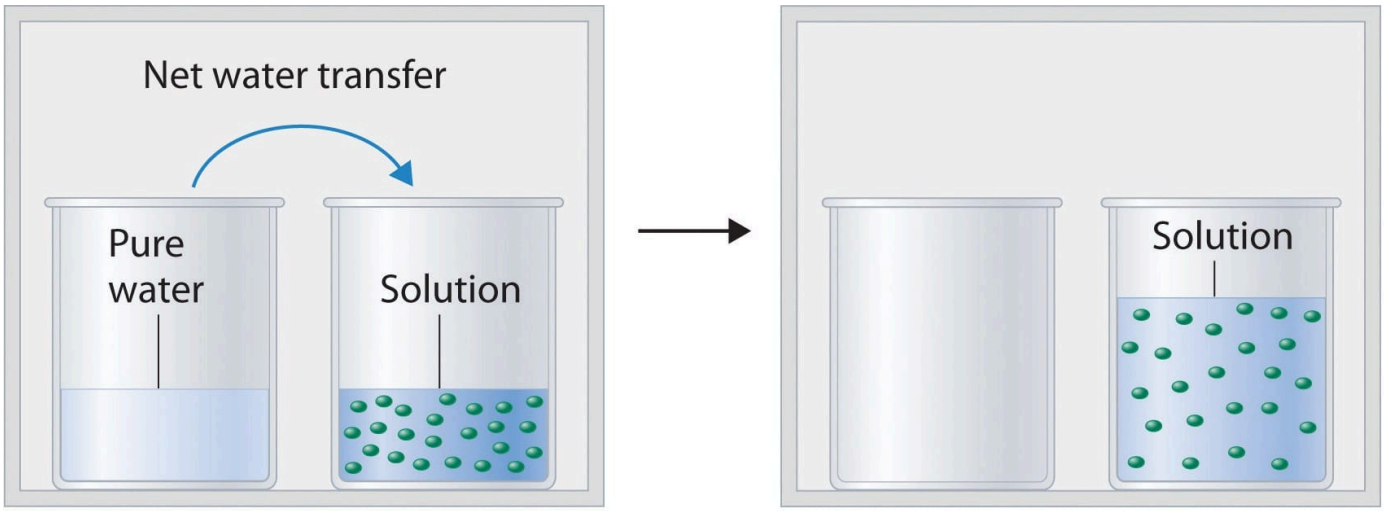


Figure 13.6.2: Transfer of Water to a Beaker Containing a Glucose Solution. (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water 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

$$P_A = X_A P_A^0 \tag{13.6.1}$$

where P_A is the vapor pressure of component A of the solution (in this case the solvent), XA is the mole fraction of A in solution, and P_A^0 is the vapor pressure of pure A. Equation 13.6.1 is known as **Raoult's law**, after the French chemist who developed it. If the solution contains only a single nonvolatile solute (B), then $X_A + X_B = 1$, and we can substitute $X_A = 1 - X_B$ to obtain

$$P_A = (1 - X_B)P_A^0 \tag{13.6.2}$$

$$= P_A^0 - X_B P_A^0 \tag{13.6.3}$$

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:

$$P_A^0 - P_A = \Delta P_A = X_B P_A^0 \tag{13.6.4}$$

We can solve vapor pressure problems in either of two ways: by using Equation 13.6.1 to calculate the actual vapor pressure above a solution of a nonvolatile solute, or by using Equation 13.6.4 to calculate the decrease in vapor pressure caused by a specified amount of a nonvolatile solute.

Example 13.6.1

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:

$$moles\ EG = (302\ \cancel{g})\left(\frac{1\ mol}{62.07\ \cancel{g}}\right) = 4.87\ mol\ EG$$

$$moles\ \mathrm{H_2O} = (698\ \cancel{g})\left(\frac{1\ mol}{18.02\ \cancel{g}}\right) = 38.7\ mol\ H_2O$$

The mole fraction of water is thus

$$X_{\mathrm{H_2O}} = \frac{38.7\ \cancel{mol}\ H_2O}{38.7\ \cancel{mol}\ H_2O + 4.87\ \cancel{mol}\ EG} = 0.888$$

B From Raoult's law (Equation 13.6.1), the vapor pressure of the solution is

$$P_{\mathrm{H_2O}} = (X_{H2_O})(P^0_{H2_O)} = (0.888)(760\ mmHg) = 675\ mmHg$$

Alternatively, we could solve this problem by calculating the mole fraction of ethylene glycol and then using Equation 13.6.4 to calculate the resulting decrease in vapor pressure:

$$X_{EG} = \frac{4.87\ mol\ EG}{4.87\ mol\ EG + 38.7\ mol\ H_2O} = 0.112$$

$$\Delta P_{\mathrm{H_2O}} = (X_{EG})(P^0_{H_2O}) = (0.112)(760\ mmHg) = 85.1\ mmHg$$

$$P_{\mathrm{H_2O}} = P^0 H_2O - \Delta P_{H_2O} = 760\ mmHg - 85.1\ mmHg = 675\ mmHg$$

The same result is obtained using either method.

Exercise 13.6.1

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.

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

Finding the Vapor Pressure of a Solution (Ionic-Nonvolatile Solute):

https://youtu.be/sRBaRXsql9s

Volatile Solutes

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_T) is the sum of the vapor pressures of the components:

$$P_T = P_A + P_B \tag{13.6.5}$$

$$= X_A P_A^0 + X_B P_B^0 \tag{13.6.6}$$

Because $X_B = 1 - X_A$ for a two-component system,

$$P_T = X_A P_A^0 + (1 - X_A) P_B^0 \tag{13.6.7}$$

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

$$P_{C_6H_6} = X_{C_6H_6} P^0_{C_6H_6} \tag{13.6.8}$$

and the vapor pressure of toluene in the solution is

$$P_{C_6H_5CH_3} = X_{C_6H_5CH_3} P^0_{C_6H_5CH3} \tag{13.6.9}$$

Equations 13.6.8 and 13.6.9 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 Figure 13.6.3. 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.

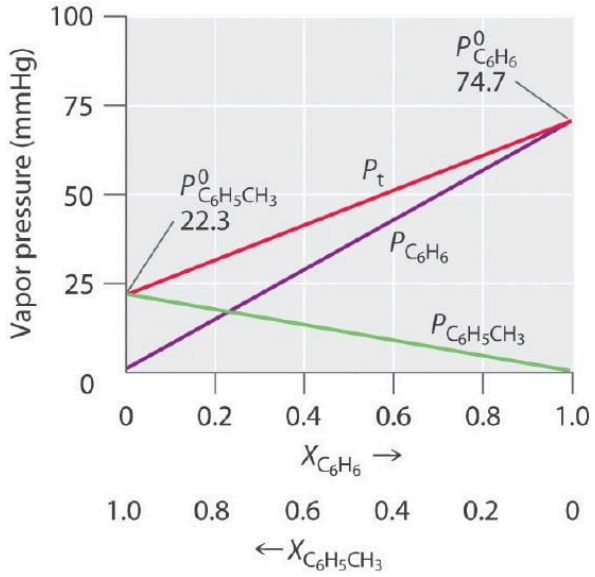


Figure 13.6.3: Vapor Pressures of Benzene–Toluene Solutions. Plots of the vapor pressures of benzene (C_6H_6) and toluene ($C_6H_5CH_3$) versus the mole fractions at 20°C are straight lines. For a solution like this, which approximates an ideal solution, the total vapor pressure of the solution (Pt) is the sum of the vapor pressures of the components.

A solution of two volatile components that behaves like the solution in Figure 13.6.3, 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 13.6.2

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

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 13.6.2

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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Finding Vapor Pressure of a Solution (Nonionic-Volatile Solute):

https://youtu.be/s06fzZZtLl0

Summary

- **Henry's law:**

$$C = kP$$

- **Raoult's law**:

$$P_A = X_A P_A^0$$

- **vapor pressure lowering**:

$$P_A^0 - P_A = \Delta P_A = X_B P_A^0$$

- **vapor pressure of a system containing two volatile components**:

$$P_T = X_A P_A^0 + (1 - X_A) P_B^0$$

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.

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

Answers

Exercise 13.6.1

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 13.6.2

approximately equal
positive deviation (vapor pressure greater than predicted)
negative deviation (vapor pressure less than predicted)

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13.7: Osmotic Pressure

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.

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 $13.7.1$, 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.

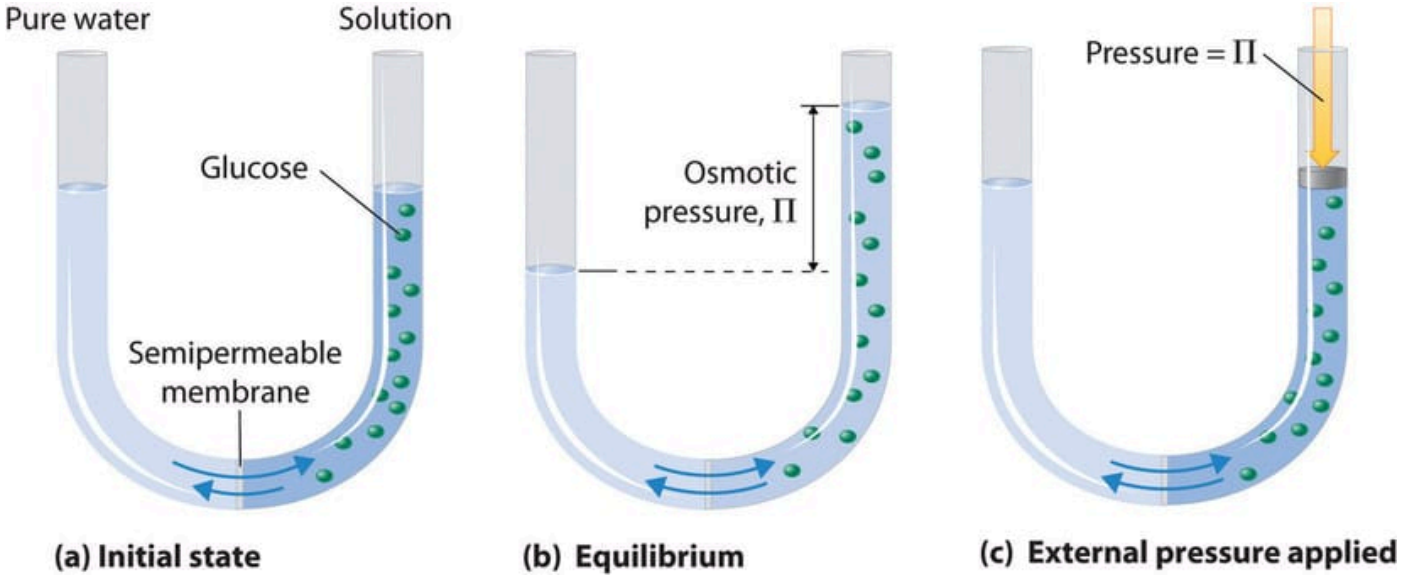


Figure $13.7.1$: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (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.*

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:

$$\Pi = \frac{nRT}{V} = MRT \tag{13.7.1}$$

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 13.7.1, osmotic pressures tend to be quite high, even for rather dilute solutions.

Example 13.7.1: Yeast Cells

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.

Calculate the osmotic pressure of a 4.0% aqueous $NaCl$ solution at 25°C.

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 13.7.1 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 13.7.1 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:

$$\begin{aligned} M_{NaCl} &= \frac{moles\ NaCl}{\text{liter solution}} \\ &= \left(\frac{4.0\ \cancel{g}\ NaCl}{58.44\ \cancel{g}/mol\ NaCl}\right)\left(\frac{1}{100\ \cancel{g\ solution}}\right)\left(\frac{1.02\ \cancel{g\ solution}}{1.00\ \cancel{mL}\ solution}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) \\ &= 0.70\ M\ NaCl \end{aligned}$$

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 13.7.1 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 13.7.1 for the molarity corresponding to this osmotic pressure:

$$M = \frac{\Pi}{RT}$$

$$= \frac{27\ \cancel{atm}}{[0.0821(L \cdot \cancel{atm})/(\cancel{K} \cdot mol)](298\ \cancel{K})}$$

$$= 1.1\ M\ glycerol$$

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 13.7.1

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: 24 atm

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 13.7.2, 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.

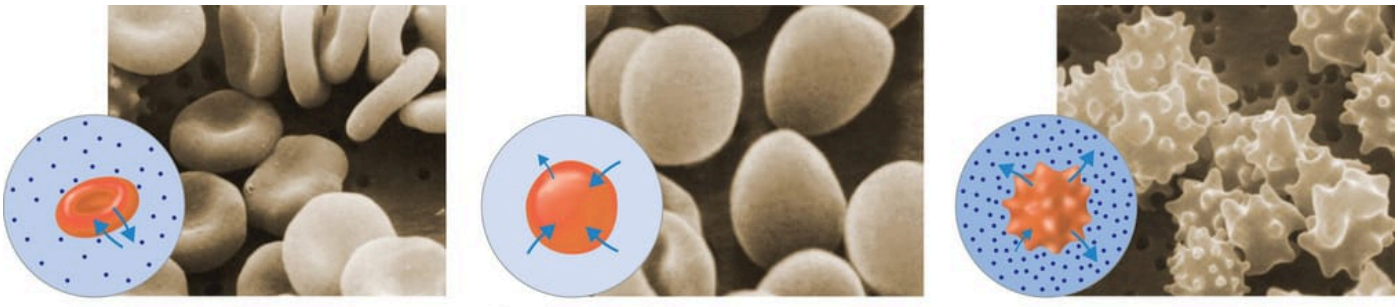


Figure 13.7.2: Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not 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 13.7.3, 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.

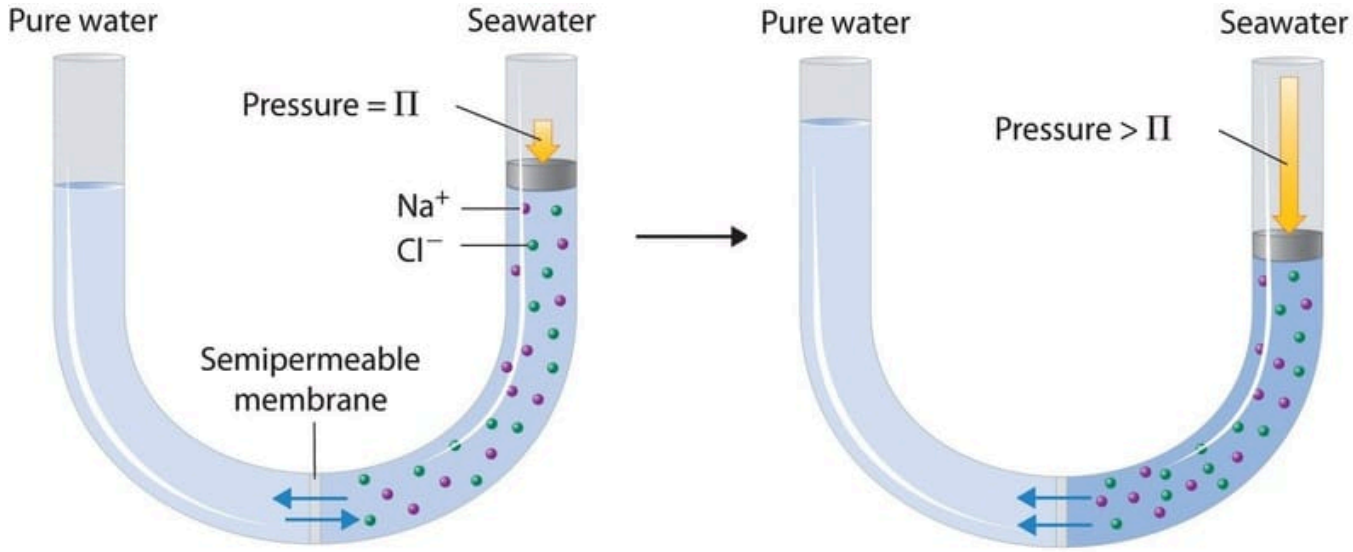


Figure 13.7.3: Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure (Π_{soln}), *there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces 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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Osmotic Pressure: https://youtu.be/uYQxI4mi3DA

Summary

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.

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13.8: Freezing-Point Depression and Boiling-Point Elevation of Nonelectrolyte Solutions

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.

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 Na+ ions and 0.01 M Cl^- ions, for a total particle concentration of 0.02 M. Similarly, the $\mathrm{CaCl_2}$ solution contains 0.01 M Ca^{2+} ions and 0.02 M 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 Mg^{2+} or 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.

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 $13.8.1$). 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.

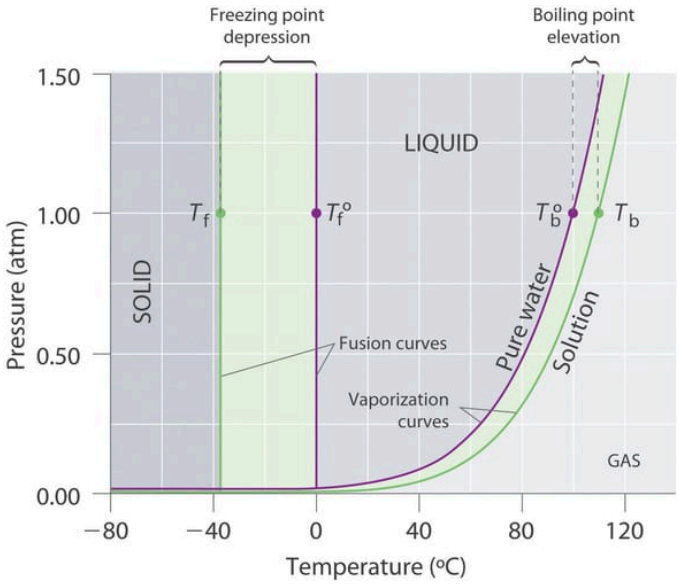


Figure 13.8.1: Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute. The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution.

> 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 13.8.2). We can define the boiling point elevation (ΔT_b) as the difference between the boiling points of the solution and the pure solvent:

$$\Delta T_b = T_b - T_b^0 \tag{13.8.1}$$

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

$$\Delta T_b = mK_b \tag{13.8.2}$$

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 13.8.1 lists characteristic Kb values for several commonly used solvents.

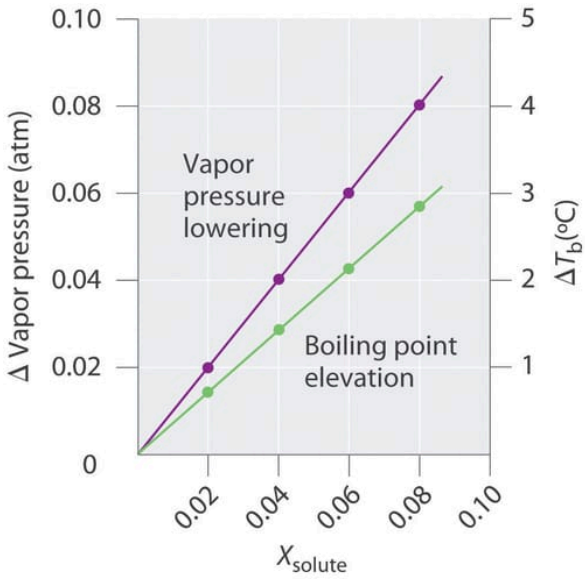


Figure 13.8.2: Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute

For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

Table 13.8.1: 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 13.8.1, 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 13.8.3

In Example 13.8.1, 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 13.8.2 to calculate the increase in boiling point.

Solution:

From Example 13.8.1, 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

$$\text{molality of ethylene glycol} = \left(\frac{4.87\ mol}{698\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.98m \tag{13.8.3}$$

From Equation 13.8.2, the increase in boiling point is therefore

$$\Delta T_b = mK_b = (6.98\ \cancel{m})(0.51°C/\cancel{m}) = 3.6°C \tag{13.8.4}$$

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 13.8.2 may not be valid.

Exercise 13.8.3

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.

Freezing Point Depression

The phase diagram in Figure 13.8.1 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.

This phenomenon is exploited in “de-icing” schemes that use salt (Figure 13.8.3), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).



Figure 13.8.3: Rock salt (NaCl), calcium chloride ($CaCl_2$), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

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:

$$\Delta T_f = T_f^0 - T_f \tag{13.8.5}$$

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 13.8.1 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 13.8.2:

$$\Delta T_f = mK_f \tag{13.8.6}$$

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 (Table 13.8.1). 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, 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. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft (Video 13.8.1).

YouTube Video

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Video 13.8.1***:*** *Freezing point depression is exploited to remove ice from the control surfaces of aircraft.*

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 13.8.4

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 Figure 13.9 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.

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 Figure 13.9. 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 13.8.4 to calculate the freezing point depressions of the solutions.

Solution:

A From Figure 13.9, 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

$$m_{\mathrm{NaCl}} = \left(\frac{36\ \cancel{g\ NaCl}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ NaCl}{58.44\ \cancel{g\ NaCl}}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.2\ m \tag{13.8.7}$$

$$m_{\mathrm{CaCl_2}} = \left(\frac{60\ \cancel{g\ CaCl_2}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ CaCl_2}{110.98\ \cancel{g\ CaCl_2}}\right)\left(\frac{1000\ \cancel{g}}{1kg}\right) = 5.4\ m \tag{13.8.8}$$

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 $\mathrm{CaCl_2}$.

B Because these salts are ionic compounds that dissociate in water to yield two and three ions per formula unit of NaCl and $\mathrm{CaCl_2}$, 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 $\mathrm{CaCl_2}$. The resulting freezing point depressions can be calculated using Equation 13.8.4:

$$\mathrm{NaCl}: \Delta T_f = mK_f = (12\ \cancel{m})(1.86°C/\cancel{m}) = 22°C \tag{13.8.9}$$

$$\mathrm{CaCl_2}: \Delta T_f = mK_f = (16\ \cancel{m})(1.86°C/\cancel{m}) = 30°C \tag{13.8.10}$$

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 $\mathrm{CaCl_2}$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $\mathrm{CaCl_2}$ 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 13.8.4

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Example 13.8.6.8 and Example 13.8.6.10.

Answer available at the end of this section.

Example 13.8.5

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, $SrCl_2$, 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 > $SrCl_2$.

Exercise 13.8.5

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.

YouTube Video

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Boiling Point Elevation and Freezing Point Depression: https://youtu.be/0MZm1Ay6LhU

Determination of Molar Masses

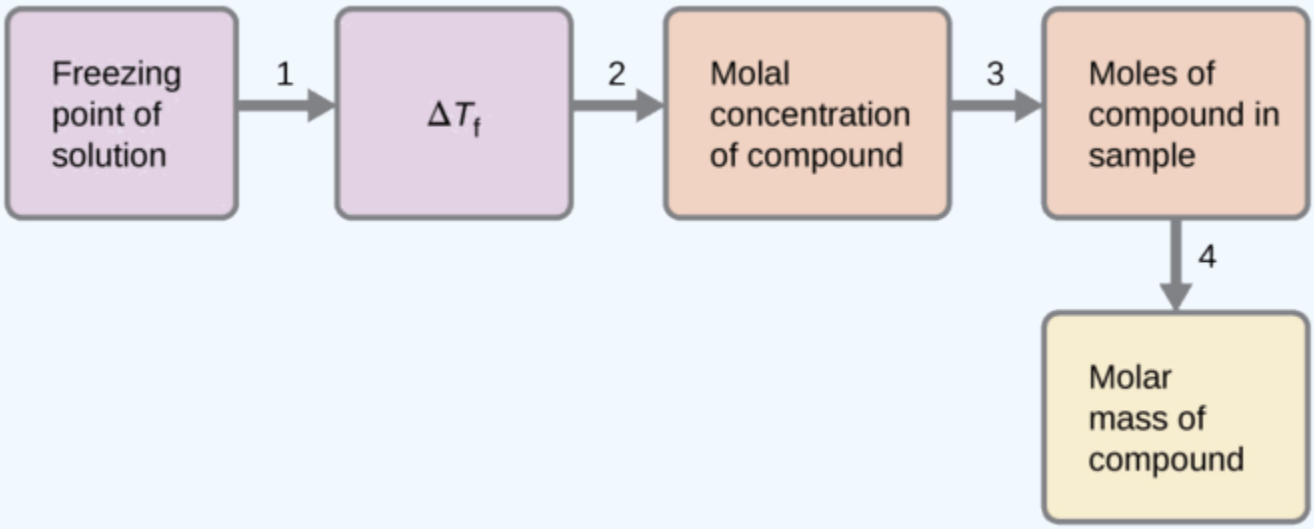
Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the concentration of solute present. Consequently, we can use a measurement of one of these properties to determine the molar mass of the solute from the measurements.

Determining Molar Mass from Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. What is the molar mass of this compound?

Solution

We can solve this problem using the following steps.



1. *Determine the change in freezing point from the observed freezing point and the freezing point of pure benzene* (Table 13.8.1).

$\Delta T_f = 5.5\ ^\circ\text{C} - 2.32\ ^\circ\text{C} = 3.2\ ^\circ\text{C}$

- *Determine the molal concentration from K_f, the freezing point depression constant for benzene* (Table 13.8.1), *and* ΔT_f.

  $\Delta T_f = K_f m$

$$m = \frac{\Delta T_f}{K_f} = \frac{3.2\ ^\circ\text{C}}{5.12\ ^\circ\text{C}m^{-1}} = 0.63\ m$$

- *Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution.*

$$\text{Moles of solute} = \frac{0.62\ \text{mol solute}}{1.00\ \cancel{\text{kg solvent}}} \times 0.0550\ \cancel{\text{kg solvent}} = 0.035\ \text{mol}$$

- *Determine the molar mass from the mass of the solute and the number of moles in that mass.*

$$\text{Molar mass} = \frac{4.00\ \text{g}}{0.034\ \text{mol}} = 1.2 \times 10^2\ \text{g/mol}$$

Exercise 13.8.6

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5 °C. What is the molar mass of this compound?

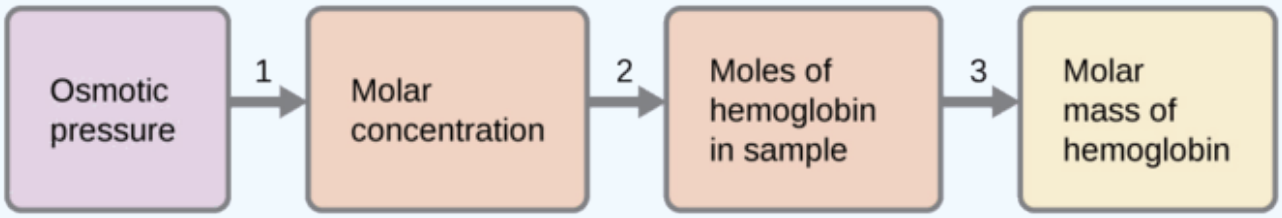
Answer available at the end of this section.

Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. What is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



1. *Convert the osmotic pressure to atmospheres, then determine the molar concentration from the osmotic pressure.*

$$\Pi = \frac{5.9\ \text{torr} \times 1\ \text{atm}}{760\ \text{torr}} = 7.8 \times 10^{-3}\ \text{atm} \tag{13.8.11}$$

$$\Pi = MRT \tag{13.8.12}$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3}\ \text{atm}}{(0.08206\ \text{L atm/mol K})(295\ \text{K})} = 3.2 \times 10^{-4}\ \text{M}$$

- *Determine the number of moles of hemoglobin in the solution from the concentration and the volume of the solution.*

$$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4}\ \text{mol}}{1\ \cancel{\text{L solution}}} \times 0.500\ \cancel{\text{L solution}} = 1.6 \times 10^{-4}\ \text{mol}$$

- *Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.*

$$\text{molar mass} = \frac{10.0\ \text{g}}{1.6 \times 10^{-4}\ \text{mol}} = 6.2 \times 10^{4}\ \text{g/mol}$$

Exercise 13.8.7

What is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

Answer available at the end of this section.

YouTube Video

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Finding the Molecular Weight of an Unknown using Colligative Properties:

https://youtu.be/faSk2REYy74

Summary

- **vapor pressure lowering**:

$$P_A^0 - P_A = \Delta P_A = X_B P_A^0 \tag{13.8.13}$$

- **vapor pressure of a system containing two volatile components**:

$$P_T = X_A P_A^0 + (1 - X_A) P_B^0 \tag{13.8.14}$$

- **boiling point elevation**:

$$\Delta T_b = m K_b \tag{13.8.15}$$

- **freezing point depression:**

$$\Delta T_f = m K_f \tag{13.8.16}$$

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.

Answers

Exercise 13.8.3

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 13.8.4

–13.0°C

Exercise 13.8.5

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 13.8.6

1.8×10^2 g/mol

Exercise 13.8.7

2.7×10^4 g/mol

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13.9: Solutions of Electrolytes

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: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.

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}} \tag{13.9.1}$$

> 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 13.9.1 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 13.9.1: 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 13.9.1). 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.

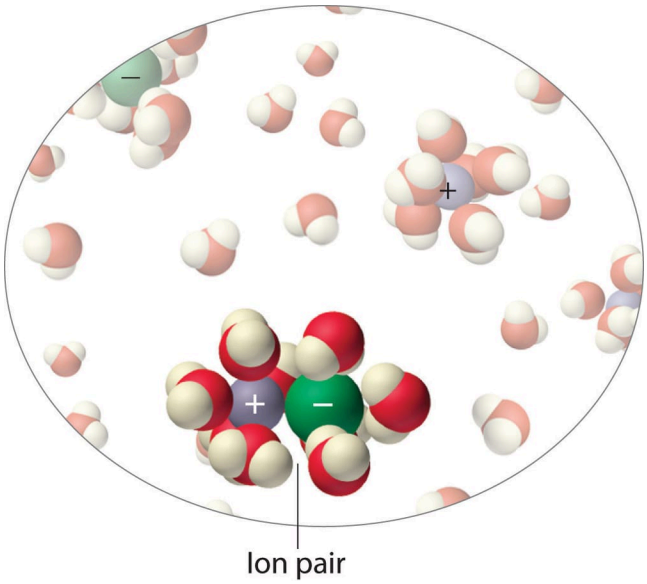


Figure 13.9.1: Ion Pairs. In concentrated solutions of electrolytes like $NaCl$, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles.

Example 13.9.1: 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 13.9.12 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 13.9.1 to calculate the van't Hoff factor.

Solution:

A If $FeCl_3$ 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

$$\Pi = MRT = (0.200\ mol/L)\,[0.0821\ (L \cdot atm)/(K \cdot mol)]\,(298\ K) = 4.89\ atm \tag{13.9.2}$$

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 $FeCl_3$ dissolved. Alternatively, we can calculate the observed particle concentration from the osmotic pressure of 4.15 atm:

$$4.15\ atm = M\,[0.0821\ (L \cdot atm)/(K \cdot mol)]\,(298\ K) \tag{13.9.3}$$

$$0.170 mol/L = M \tag{13.9.4}$$

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 $FeCl_3$ dissolved. From Equation 13.9.1, the van't Hoff factor for the solution is

$$i = \frac{3.40 \text{ particles observed}}{1 \text{ formula unit } FeCl_3} = 3.40 \tag{13.9.5}$$

Exercise 13.9.1: 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:

2.7 (versus an ideal value of 3

Key Concepts and Summary

Ionic compounds may not completely dissociate in solution due to **activity** effects, in which case observed colligative effects may be less than predicted.

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13.10: Colloidal Mixtures

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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14: CHEMICAL KINETICS

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

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14.1: The Rate of a Chemical Reaction

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.

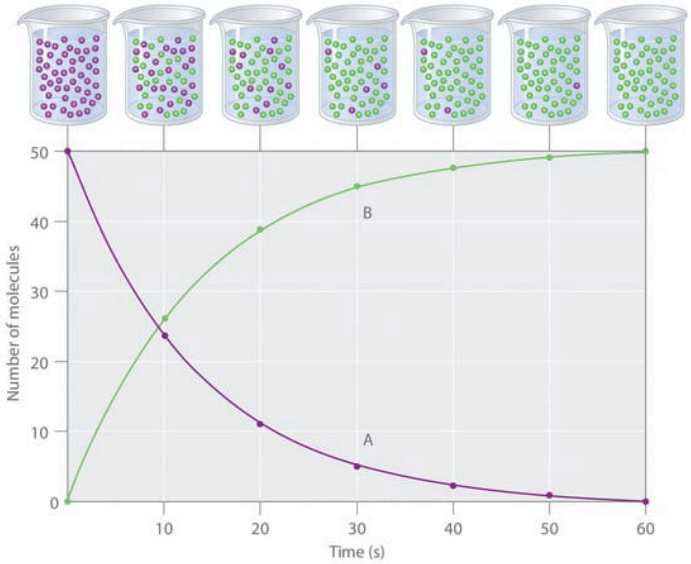


Figure 14.1.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure 14.1.1; 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 14.1.1. 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.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{14.1.1}$$

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 14.1.1 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.

YouTube Video

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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 14.1.1 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 14.1.2.

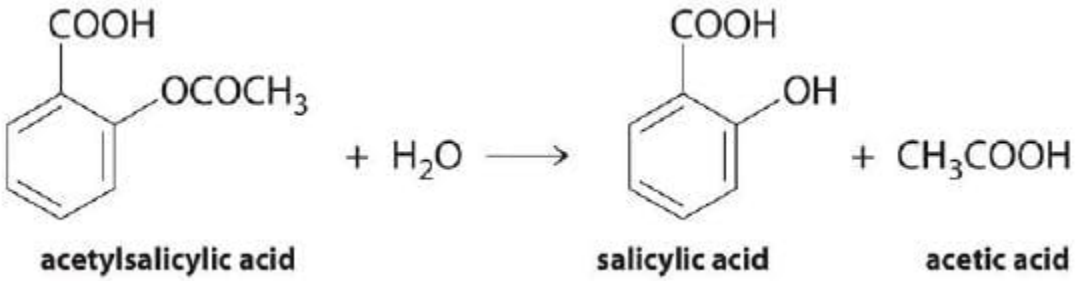


Figure 14.1.2: Hydrolysis of Aspirin reaction.

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 14.1.1 and are shown in the graph in Figure 14.1.3.

*Table 14.1.1: 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 14.1.1 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).

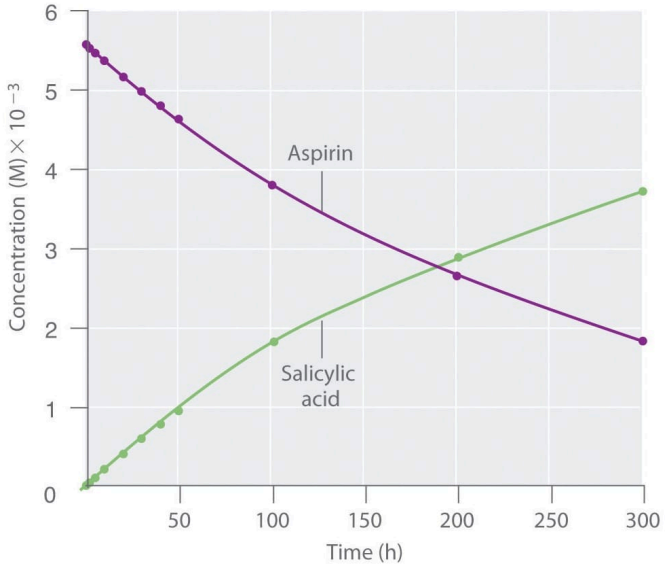


Figure 14.1.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, 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 14.1.1(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:

$$\underset{\text{sucrose}}{\mathrm{C_{12}H_{22}O_{11}(aq)}} + \mathrm{H_2O(l)} \rightarrow 4\mathrm{C_2H_5OH(aq)} + 4\mathrm{CO_2(g)} \tag{14.1.2}$$

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:

$$\frac{\Delta[\mathrm{C_2H_5OH}]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{14.1.3}$$

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 14.1.3 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 14.1.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[\mathrm{C_2H_5OH}]}{\Delta t}\right) \tag{14.1.4}$$

Example 14.1.1: 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 14.1.1: 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 14.1.2: Decomposition Reaction II

Using the reaction shown in Example 14.1.1, 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 14.1.1, 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 14.1.1, 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 14.1.2: 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 14.1.1**: 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 14.1.2**: Contact Process II**

9.0×10^{-6} M/s

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14.2: Measuring Reaction Rates

The method for determining a reaction rate is relatively straightforward. Since a reaction rate is based on change over time, it must be determined from tabulated values or found experimentally. With the obtained data, it is possible to calculate the reaction rate either algebraically or graphically. What follows is general guidance and examples of measuring the rates of a reaction. Measuring time change is easy; a stopwatch or any other time device is sufficient. However, determining the change in concentration of the reactants or products involves more complicated processes. The change of concentration in a system can generally be acquired in two ways:

1. By monitoring the depletion of reactant over time, or
2. By monitoring the formation of product over time

It does not matter whether an experimenter monitors the reagents or products because there is no effect on the overall reaction. However, since reagents decrease during reaction, and products increase, there is a sign difference between the two rates. Reagent concentration decreases as the reaction proceeds, giving a negative number for the change in concentration. The products, on the other hand, increase concentration with time, giving a positive number. Since the convention is to express the rate of reaction as a positive number, to solve a problem, set the overall rate of the reaction equal to the negative of a reagent's disappearing rate. The overall rate also depends on stoichiometric coefficients.

It is worth noting that the process of measuring the concentration can be greatly simplified by taking advantage of the different physical or chemical properties (ie: phase difference, reduction potential, etc.) of the reagents or products involved in the reaction by using the above methods. We have emphasized the importance of taking the sign of the reaction into account to get a positive reaction rate. Now, we will turn our attention to the importance of stoichiometric coefficients.

A reaction rate can be reported quite differently depending on which product or reagent selected to be monitored.

Given a reaction:

$$aA + bB \rightarrow cC + dD \tag{14.2.1}$$

the general rate for this reaction is defined as

$$rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} \tag{14.2.2}$$

Equation 14.2.2 can also be written as:

rate of reaction = $-\frac{1}{a}$ (rate of disappearance of A)

= $-\frac{1}{b}$ (rate of disappearance of B)

= $\frac{1}{c}$ (rate of formation of C)

= $\frac{1}{d}$ (rate of formation of D)

Even though the concentrations of A, B, C and D may all change at different rates, there is only one average rate of reaction. To get this unique rate, choose any one rate and divide it by the stoichiometric coefficient. When the reaction has the formula:

$$C_{R1}R_1 + \cdots + C_{Rn}R_n \rightarrow C_{P1}P_1 + \cdots + C_{Pn}P_n \tag{14.2.3}$$

The general case of the unique average rate of reaction has the form:

$$\text{rate of reaction} = -\frac{1}{C_{R1}}\frac{\Delta[R_1]}{\Delta t} = \cdots = -\frac{1}{C_{Rn}}\frac{\Delta[R_n]}{\Delta t} = \frac{1}{C_{P1}}\frac{\Delta[P_1]}{\Delta t} = \cdots = \frac{1}{C_{Pn}}\frac{\Delta[P_n]}{\Delta t}$$

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Average Reaction Rates: https://youtu.be/jc6jntB7GHk

Following the Course of a Reaction

Rather than performing a whole set of initial rate experiments, one can gather information about orders of reaction by following a particular reaction from start to finish. There are two different ways this can be accomplished.

1. Samples of the mixture can be collected at intervals and titrated to determine how the concentration of one of the reagents is changing.
2. A physical property of the reaction which changes as the reaction continues can be measured: for example, the volume of gas produced.

These approaches must be considered separately.

Consider that bromoethane reacts with sodium hydroxide solution as follows:

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^- \tag{14.2.4}$$

During the course of the reaction, both bromoethane and sodium hydroxide are consumed. However, it is relatively easy to measure the concentration of sodium hydroxide at any one time by performing a titration with a standard acid: for example, with hydrochloric acid of a known concentration.

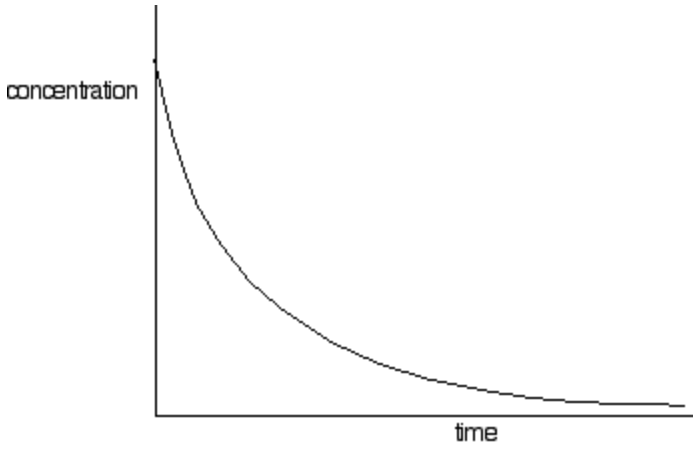
The process starts with known concentrations of sodium hydroxide and bromoethane, and it is often convenient for them to be equal. Because the reaction is 1:1, if the concentrations are equal at the start, they remain equal throughout the reaction. Samples are taken with a pipette at regular intervals during the reaction, and titrated with standard hydrochloric acid in the presence of a suitable indicator. The problem with this approach is that the reaction is still proceeding in the time required for the titration. In addition, only one titration attempt is possible, because by the time another sample is taken, the concentrations have changed.

There are two ways around this problem:

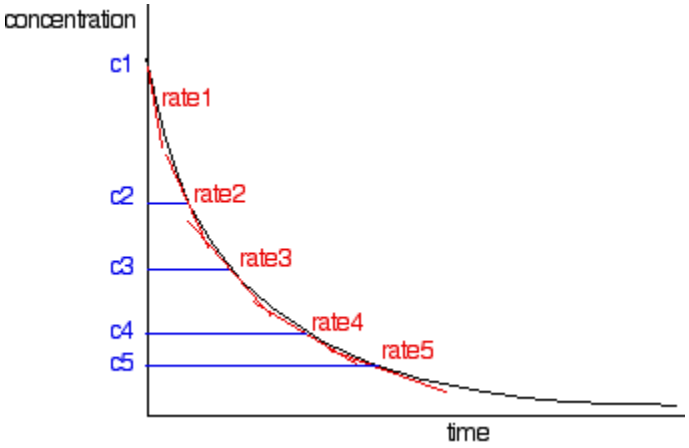
1. The reaction can be slowed by diluting it, adding the sample to a larger volume of cold water before the titration. Then the titration is performed as quickly as possible. This is most effective if the reaction is carried out above room temperature. Cooling it as well as diluting it slows it down even more.
2. If possible (and it is possible in this case) it is better to stop the reaction completely before titrating. In this case, this can be accomplished by adding the sample to a known, excess volume of standard hydrochloric acid. This consumes all the sodium hydroxide in the mixture, stopping the reaction.

At this point the resulting solution is titrated with standard sodium hydroxide solution to determine how much hydrochloric acid is left over in the mixture. This allows one to calculate how much acid was used, and thus how much sodium hydroxide must have been present in the original reaction mixture. This technique is known as a **back titration**.

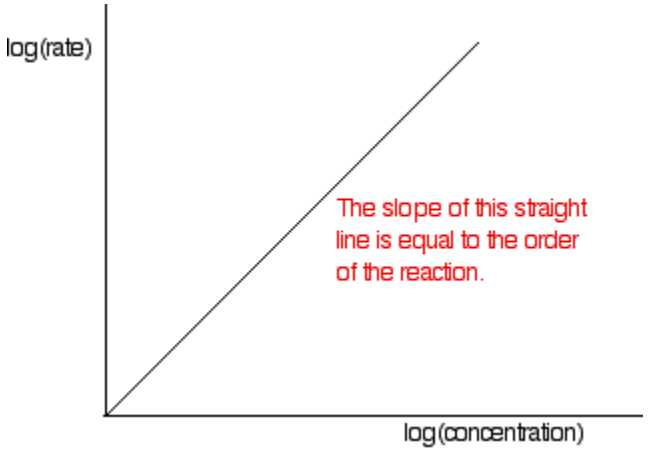
This process generates a set of values for concentration of (in this example) sodium hydroxide over time. The concentrations of bromoethane are, of course, the same as those obtained if the same concentrations of each reagent were used. These values are plotted to give a concentration-time graph, such as that below:



The rates of reaction at a number of points on the graph must be calculated; this is done by drawing tangents to the graph and measuring their slopes.



These values are then tabulated. The quickest way to proceed from here is to plot a log graph as described further up the page. All rates are converted to log(rate), and all the concentrations to log(concentration). Then, log(rate) is plotted against log(concentration). The slope of the graph is equal to the order of reaction.



In the example of the reaction between bromoethane and sodium hydroxide solution, the order is calculated to be 2. Notice that this is the overall order of the reaction, not just the order with respect to the reagent whose concentration was measured. The rate of reaction decreases because the concentrations of both of the reactants decrease.

Example 14.2.1: The course of the reaction

A familiar example is the catalytic decomposition of hydrogen peroxide (used above as an example of an initial rate experiment).

$$2H_2O_{2(aq)} \xrightarrow{MnO_{2(s)}} 2H_2O_{(l)} + O_{2(g)}$$

This time, measure the oxygen given off using a gas syringe, recording the volume of oxygen collected at regular intervals.

The practical side of this experiment is straightforward, but the calculation is not. The problem is that the volume of the product is measured, whereas the concentration of the reactants is used to find the reaction order. This means that the concentration of hydrogen peroxide remaining in the solution must be determined for each volume of oxygen recorded. This requires ideal gas law and stoichiometric calculations.

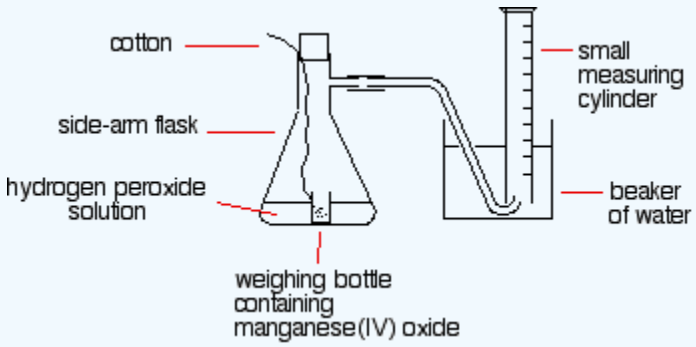
The table of concentrations and times is processed as described above.

Example 14.2.2: The catalytic decomposition of hydrogen peroxide

This is an example of measuring the initial rate of a reaction producing a gas.

$$2H_2O_{2(aq)} \xrightarrow{MnO_{2(s)}} 2H_2O_{(l)} + O_{2(g)}$$

A simple set-up for this process is given below:



The reason for the weighing bottle containing the catalyst is to avoid introducing errors at the beginning of the experiment. The catalyst must be added to the hydrogen peroxide solution without changing the volume of gas collected. If it is added to the flask using a spatula before replacing the bung, some gas might leak out before the bung is replaced. Alternatively, air might be forced into the measuring cylinder. Either would render results meaningless.

To start the reaction, the flask is shaken until the weighing bottle falls over, and then shaken further to make sure the catalyst mixes evenly with the solution. Alternatively, a special flask with a divided bottom could be used, with the catalyst in one side and the hydrogen peroxide solution in the other. The two are easily mixed by tipping the flask. Using a 10 cm^3 measuring cylinder, initially full of water, the time taken to collect a small fixed volume of gas can be accurately recorded. A small gas syringe could also be used.

To study the effect of the concentration of hydrogen peroxide on the rate, the concentration of hydrogen peroxide must be changed and everything else held constant—the temperature, the total volume of the solution, and the mass of manganese(IV) oxide. The manganese(IV) oxide must also always come from the same bottle so that its state of division is always the same.

The same apparatus can be used to determine the effects of varying the temperature, catalyst mass, or state of division due to the catalyst

Example 14.2.3: The thiosulphate-acid reaction

Mixing dilute hydrochloric acid with sodium thiosulphate solution causes the slow formation of a pale yellow precipitate of sulfur.

$$Na_2S_2O_{2(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + S_{(s)} + SO_{2(g)} \tag{14.2.5}$$

A very simple, but very effective, way of measuring the time taken for a small fixed amount of precipitate to form is to stand the flask on a piece of paper with a cross drawn on it, and then look down through the solution until the cross disappears.

A known volume of sodium thiosulphate solution is placed in a flask. Then a small known volume of dilute hydrochloric acid is added, a timer is started, the flask is swirled to mix the reagents, and the flask is placed on the paper with the cross. The timer is used to determine the time for the cross to disappear. The process is repeated using a smaller volume of sodium thiosulphate, but topped up to the same original volume with water. Everything else is exactly as before.

The actual concentration of the sodium thiosulphate does not need to be known. In each case the relative concentration could be recorded. The solution with 40 cm^3 of sodium thiosulphate solution plus 10 cm^3 of water has a concentration which is 80% of the original, for example. The one with 10 cm^3 of sodium thiosulphate solution plus 40 cm^3 of water has a concentration 20% of the original.

The quantity 1/t can again be plotted as a measure of the rate, and the volume of sodium thiosulphate solution as a measure of concentration. Alternatively, relative concentrations could be plotted. In either case, the shape of the graph is the same.

The effect of temperature on this reaction can be measured by warming the sodium thiosulphate solution before adding the acid. The temperature must be measured after adding the acid, because the cold acid cools the solution slightly.This time, the temperature is changed between experiments, keeping everything else constant. To get reasonable times, a diluted version of the sodium thiosulphate solution must be used. Using the full strength, hot solution produces enough precipitate to hide the cross almost instantly.

Example 14.2.4: The Iodine Clock Reactions

There are several reactions bearing the name "iodine clock." Each produces iodine as one of the products. This is the simplest of them, because it involves the most familiar reagents.

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The reaction below is the oxidation of iodide ions by hydrogen peroxide under acidic conditions:

$$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+ \rightarrow I_{2(aq)} + 2H_2O_{(l)} \tag{14.2.6}$$

The iodine is formed first as a pale yellow solution, darkening to orange and then dark red before dark gray solid iodine is precipitated.

Iodine reacts with starch solution to give a deep blue solution. If starch solution is added to the reaction above, as soon as the first trace of iodine is formed, the solution turns blue. This gives no useful information. However, iodine also reacts with sodium thiosulphate solution:

$$2S_2O^{2-}_{3(aq)} + I_{2(aq)} \rightarrow S_2O^{2-}_{6(aq)} + 2I^-_{(aq)} \tag{14.2.7}$$

If a very small amount of sodium thiosulphate solution is added to the reaction mixture (including the starch solution), it reacts with the iodine that is initially produced, so the iodine does not affect the starch, and there is no blue color. However, when that small amount of sodium thiosulphate is consumed, nothing inhibits further iodine produced from reacting with the starch. The mixture turns blue.

Average vs. Instantaneous Reaction Rates

Reaction rates have the general form of (change of concentration / change of time). There are two types of reaction rates. One is called the average rate of reaction, often denoted by (Δ[conc.] / Δt), while the other is referred to as the instantaneous rate of reaction, denoted as either:

$$\lim_{\Delta t \to 0} \frac{\Delta[concentration]}{\Delta t} \tag{14.2.8}$$

or

$$\frac{d[concentration]}{dt} \tag{14.2.9}$$

The average rate of reaction, as the name suggests, is an average rate, obtained by taking the change in concentration over a time period, for example: -0.3 M / 15 minutes. This is an approximation of the reaction rate in the interval; it does not necessarily mean that the reaction has this specific rate throughout the time interval or even at any instant during that time. The instantaneous rate of reaction, on the other hand, depicts a more accurate value. The instantaneous rate of reaction is defined as the change in concentration of an infinitely small time interval, expressed as the limit or derivative expression above. Instantaneous rate can be obtained from the experimental data by first graphing the concentration of a system as function of time, and then finding the slope of the tangent line at a specific point which corresponds to a time of interest. Alternatively, experimenters can measure the change in concentration over a very small time period two or more times to get an average rate close to that of the instantaneous rate. The reaction rate for that time is determined from the slope of the tangent lines.

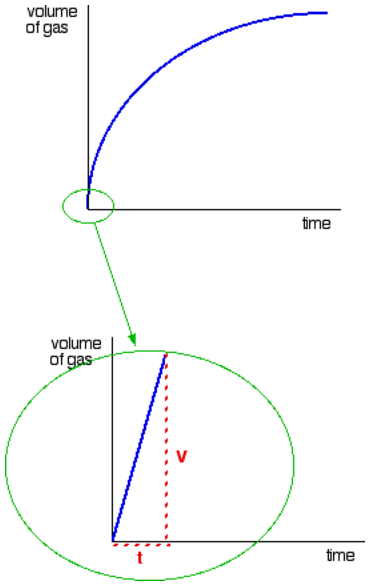
Initial Rate of Reaction

The initial rate of reaction is the rate at which the reagents are first brought together. Like the instantaneous rate mentioned above, the initial rate can be obtained either experimentally or graphically. To experimentally determine the initial rate, an experimenter must bring the reagents together and measure the reaction rate as quickly as possible. If this is not possible, the experimenter can find the initial rate graphically. To do this, he must simply find the slope of the line tangent to the reaction curve when t=0.

The simplest initial rate experiments involve measuring the time taken for some recognizable event to happen early in a reaction. This could be the time required for 5 cm^3 of gas to be produced, for a small, measurable amount of precipitate to form, or for a dramatic color change to occur. Examples of these three indicators are discussed below.

The concentration of one of the components of the reaction could be changed, holding everything else constant: the concentrations of other reactants, the total volume of the solution and the temperature. The time required for the event to occur is then measured. This process is repeated for a range of concentrations of the substance of interest. A reasonably wide range of concentrations must be measured.This process could be repeated by altering a different property.

Consider a simple example of an initial rate experiment in which a gas is produced. This might be a reaction between a metal and an acid, for example, or the catalytic decomposition of hydrogen peroxide. If volume of gas evolved is plotted against time, the first graph below results.



A measure of the rate of the reaction at any point is found by measuring the slope of the graph. The steeper the slope, the faster the rate. Because the initial rate is important, the slope at the beginning is used. In the second graph, an enlarged image of the very beginning of the first curve, the curve is approximately straight. This is only a reasonable approximation when considering an early stage in the reaction. As the reaction progresses, the curvature of the graph increases. Suppose the experiment is repeated with a different (lower) concentration of the reagent. Again, the time it takes for the same volume of gas to evolve is measured, and the initial stage of the reaction is studied.

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Instantaneous Rates: https://youtu.be/GGOdoIzxvAo

Example 14.2.2

Determine the initial rate of the reaction using the table below.

Time	[A]
100	1.55
200	0.99
300	0.67
400	0.45
500	0.34
600	0.24

Solution

initial rate of reaction = $\frac{-(0-2.5)M}{(195-0)sec}$ = 0.0125 M per sec

Use the points [A]=2.43 M, t= 0 and [A]=1.55, t=100

initial rate of reaction = $-\frac{\Delta[A]}{\Delta t} = \frac{-(1.55-2.43)M}{(100-0)sec}$ = 0.0088 M per sec

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14.3: Effect of Concentration on Reaction Rates: 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.

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*.

Note

Under a given set of conditions, the value of the rate constant does not change as the reaction progresses.

Although differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, integrated rate laws are used to determine the reaction order and the value of the rate constant from experimental measurements. (Click the link for a presentation of the general forms for integrated rate laws.)

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. 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

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{14.3.4}$$

gives a general expression for the differential rate law:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^m[\text{B}]^n \tag{14.3.5}$$

Inserting the identities of the reactants into Equation 14.3.5 gives the following expression for the differential rate law for the reaction:

$$\text{rate} = -\frac{\Delta[(\text{CH}_3)_3\text{CBr}]}{\Delta t} = k[(\text{CH}_3)_3\text{CBr}]^m[\text{H}_2\text{O}]^n \tag{14.3.6}$$

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 14.3.5 are 1 and 0, respectively, and,

$$\text{rate} = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr] \tag{14.3.7}$$

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:

$$\text{rate} = -\frac{\Delta[\text{CH}_3\text{Br}]}{\Delta t} = k'[\text{CH}_3\text{Br}] \tag{14.3.8}$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 14.3.8 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. For methyl bromide, in contrast, the differential rate law becomes 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.

Note

Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements.

Example 14.3.1

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.

1. $2\mathrm{HI(g)} \xrightarrow{\mathrm{Pt}} \mathrm{H_2(g)} + \mathrm{I_2(g)}\ \text{rate} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{HI}]}{\Delta t}\right) = k[\mathrm{HI}]^2$
2. $2\mathrm{N_2O(g)} \xrightarrow{\Delta} 2\mathrm{N_2(g)} + \mathrm{O_2(g)}\ \text{rate} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{N_2O}]}{\Delta t}\right) = k$
3. $\text{cyclopropane(g)} \rightarrow \text{propane(g)}\ \text{rate} = -\frac{\Delta[\text{cyclopropane}]}{\Delta t} = k[\text{cyclopropane}]$

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** $[\mathrm{HI}]^2$ 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)]:

$$k\mathrm{M}^2 = \frac{\mathrm{M}}{\mathrm{s}}k = \frac{\mathrm{M/s}}{\mathrm{M}^2} = \frac{1}{\mathrm{M}\cdot\mathrm{s}} = \mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$$

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 $k[\mathrm{HI}]_0^2$ to $k(2[\mathrm{HI}])_0^2 = 4k[\mathrm{HI}]_0^2$. 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[cyclopropane]$_0$ to $2k$[cyclopropane]$_0$. This doubles the reaction rate.

Exercise 14.3.1

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.

$$\mathrm{CH_3N{=}NCH_3(g) \rightarrow C_2H_6(g) + N_2(g)} \tag{14.3.9}$$

with

$$\mathrm{rate} = -\frac{\Delta[\mathrm{CH_3N{=}NCH_3}]}{\Delta t} = k[\mathrm{CH_3N{=}NCH_3}] \tag{14.3.10}$$

b.

$$\mathrm{2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)} \tag{14.3.11}$$

with

$$\mathrm{rate} = -\frac{\Delta[\mathrm{F_2}]}{\Delta t} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{NO_2}]}{\Delta t}\right) = k[\mathrm{NO_2}][\mathrm{F_2}] \tag{14.3.12}$$

Answer

a. s^{-1}; first order in $CH_3N{=}NCH_3$; first order overall; doubling [$CH_3N{=}NCH_3$] will double the reaction rate.

b. $M^{-1}{\cdot}s^{-1}$; first order in NO_2, first order in F_2; second order overall; doubling [NO_2] will double the reaction rate.

Methods of Initial Rates

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:

$$\mathrm{rate} = k[A]^m[B]^n \tag{14.3.13}$$

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 14.3.13. 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 14.3.1.

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_3]^m[\text{B}_3]^n} \tag{14.3.14}$$

Inserting the appropriate values from Table 14.3.1,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{34 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[1.00\ \text{M}]^m[0.50\ \text{M}]^n} \tag{14.3.15}$$

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 14.3.1,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{8.5 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[0.50\ \text{M}]^m[1.00\ \text{M}]^n} \tag{14.3.16}$$

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 14.3.1 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 14.3.2

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:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \tag{14.3.17}$$

Determine the 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

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{7.98 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0125\ \text{M})} = 1.16 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1} \tag{14.3.18}$$

Alternatively, using Experiment 2 gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{15.9 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0250\ \text{M})} = 1.15 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1} \tag{14.3.19}$$

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 14.3.2

The peroxydisulfate ion ($S_2O_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O^{2-}_{8(aq)} + 3I^-_{(aq)} \rightarrow 2SO^{2-}_{4(aq)} + I^-_{3(aq)} \tag{14.3.20}$$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

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 rate = $k[S_2O_8^{2-}][I^-]$; $k = 20\ M^{-1}{\cdot}s^{-1}$

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Initial Rates and Rate Law Expressions: https://youtu.be/VZl5dipsCEQ

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.

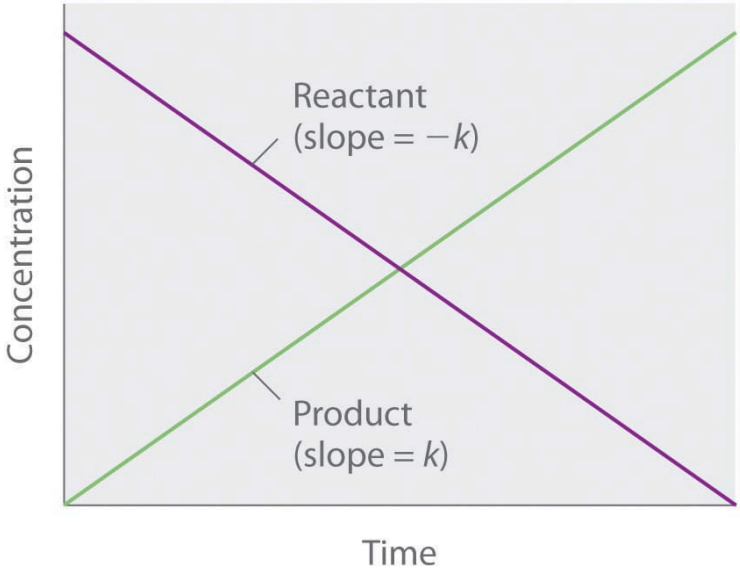
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14.4: Zero-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is 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.



The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

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* = $[A]_0$.) 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:

$$2\text{N}_2\text{O(g)} \xrightarrow{\text{Pt}} 2\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \tag{14.4.3}$$

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:

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\text{N}_2\text{O}]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[\text{N}_2]}{\Delta t}\right) = \frac{\Delta[\text{O}_2]}{\Delta t} = k[\text{N}_2\text{O}]^0 = k \tag{14.4.4}$$

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 14.4.1, 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.

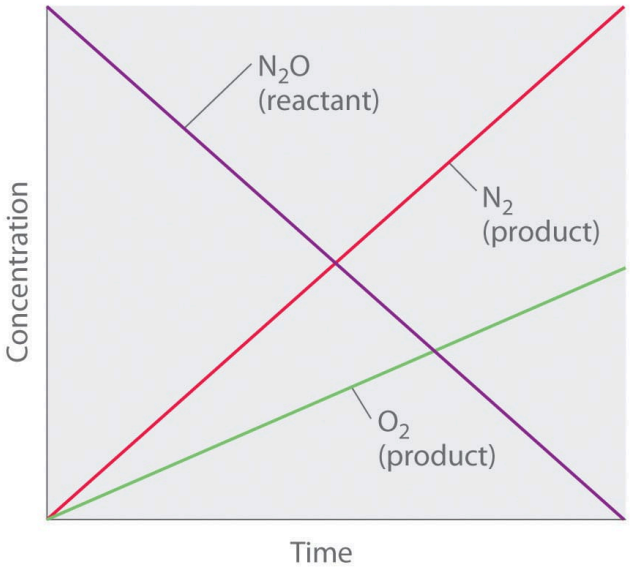


Figure 14.4.1**:** *A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.*

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

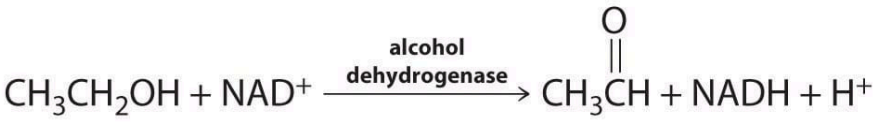


Figure 14.4.2

where 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 (part (a) in Figure 14.4.3). 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).

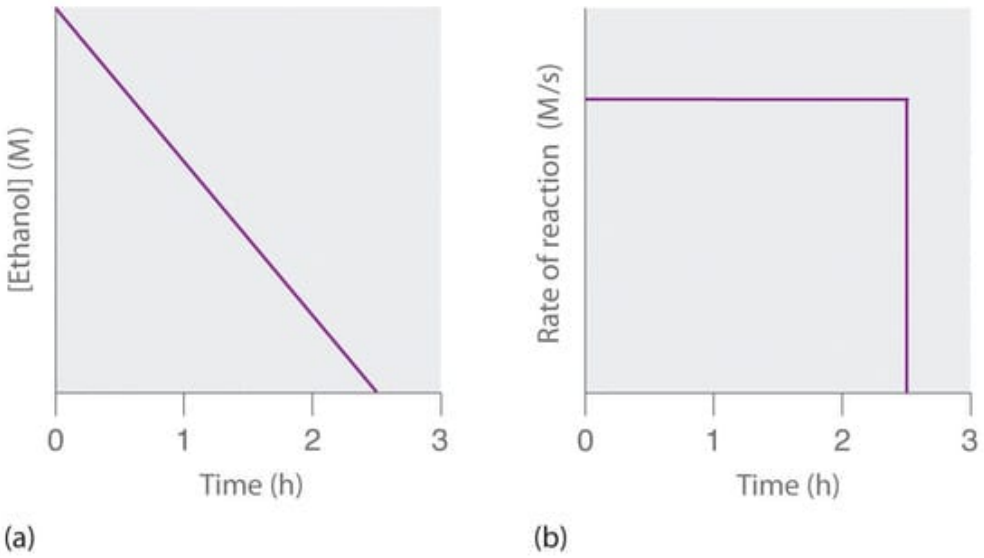


Figure 14.4.3: The Catalyzed Oxidation of Ethanol *(a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point 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.*

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14.5: 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:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \tag{14.5.1}$$

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:

$$[A] = [A]_0 e^{-kt} \tag{14.5.2}$$

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 14.5.2 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 14.5.2 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[A] = \ln [A]_0 - kt \tag{14.5.3}$$

Because Equation 14.5.3 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 14.5.1) or the integrated rate law (Equation 14.5.3) can be used to determine whether a particular reaction is first order.

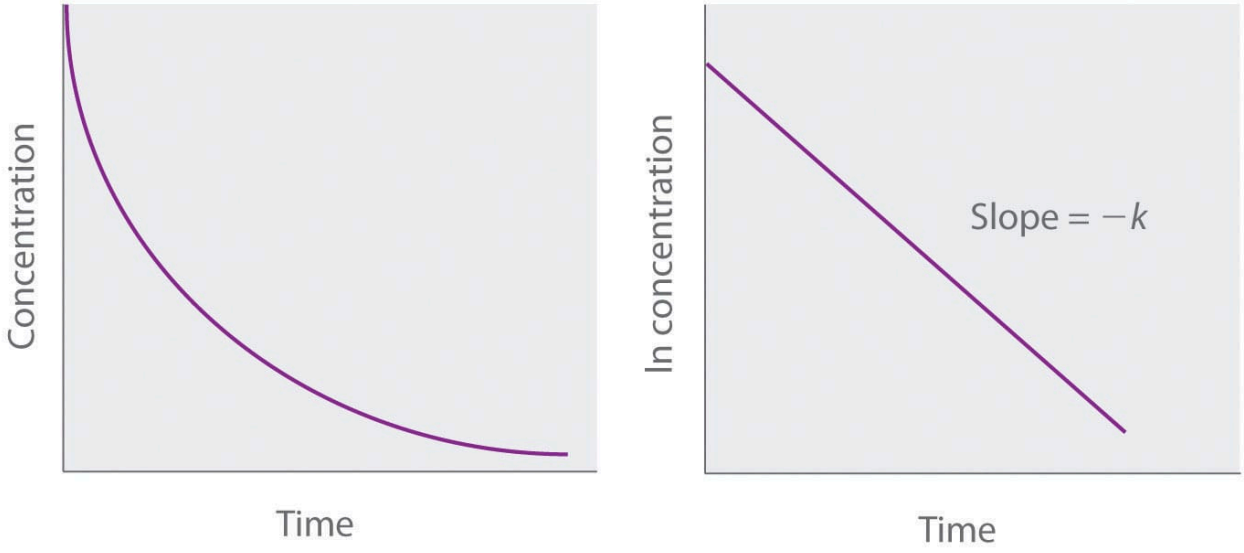


Figure 14.5.1: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. We have already encountered two examples of first-order reactions: the hydrolysis of aspirin and the reaction of *t*-butyl bromide with water to give *t*-butanol. Another 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:

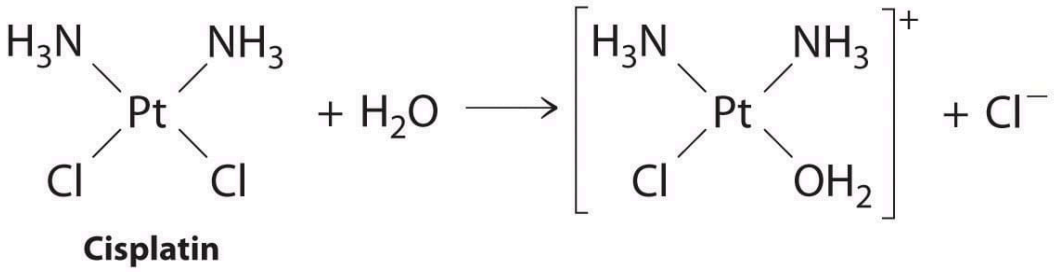


Figure 14.5.2

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 14.5.1 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 14.5.1 have been studied extensively to find ways of maximizing the concentration of the active species.

Note

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 14.5.1. 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. 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 14.5.1 shows that the reaction rate doubles [$(1.8 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ 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 [$(4.5 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ 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 14.5.1. For example, substituting the values for Experiment 3 into Equation 14.5.1,

$$3.6 \times 10^{-5} \text{ M/min} = k(0.024 \text{ M})$$

$$1.5 \times 10^{-3} \text{ min}^{-1} = k$$

Table 14.5.1: 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}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

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 14.5.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$CH_3CH_2Cl(g) \xrightarrow{\Delta} HCl(g) + C_2H_4(g)$$

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.

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 14.5.1

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.

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 first order; $k = 2.2 \times 10^{-5}\ s^{-1}$

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. Part (a) in Figure 14.5.3 shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

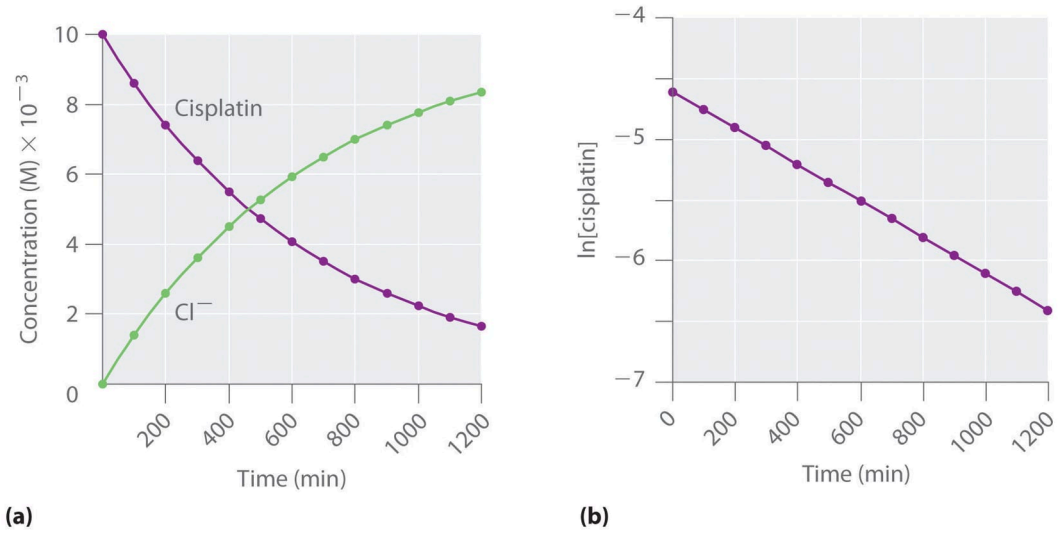


Figure 14.5.3: *The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The 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 14.5.3. 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 14.5.3 for t = 100 min ([cisplatin] = 0.0086 M) and t = 1000 min ([cisplatin] = 0.0022 M),

$$\text{slope} = \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000\ \text{min} - 100\ \text{min}} \tag{14.5.4}$$

$$-k = \frac{\ln 0.0022 - \ln 0.0086}{1000\ \text{min} - 100\ \text{min}} = \frac{-6.12 - (-4.76)}{900\ \text{min}} = -1.51 \times 10^{-3}\ \text{min}^{-1} \tag{14.5.5}$$

$$k = 1.5 \times 10^{-3}\ \text{min}^{-1} \tag{14.5.6}$$

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 14.5.3 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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The First-Order Integrated Rate Law Equation: https://youtu.be/_JskhfxBAMI

Example 14.5.2

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 14.5.2) is $[A] = [A]_0e^{-kt}$.

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,

$$[CH_3CH_2Cl]_{10\ h} = [CH_3CH_2Cl]_0e^{-kt} \tag{14.5.7}$$
$$= 0.0200\ M(e^{-(1.6\times10^{-6}\ s^{-1})[(10\ h)(60\ min/h)(60\ s/min)]}) \tag{14.5.8}$$
$$= 0.0189\ M \tag{14.5.9}$$

We could also have used the logarithmic form of the integrated rate law (Equation 14.5.3):

$$\ln [CH_3CH_2Cl]_{10\ h} = \ln [CH_3CH_2Cl]_0 - kt \tag{14.5.10}$$
$$= \ln 0.0200 - (1.6 \times 10^{-6}\ s^{-1})[(10\ h)(60\ min/h)(60\ s/min)] \tag{14.5.11}$$
$$= -3.912 - 0.0576 = -3.970 \tag{14.5.12}$$
$$[CH_3CH_2Cl]_{10\ h} = e^{-3.970}\ M \tag{14.5.13}$$
$$= 0.0189\ M \tag{14.5.14}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 14.5.3 gives the following:

$$\ln [CH_3CH_2Cl]_t = \ln [CH_3CH_2Cl]_0 - kt \tag{14.5.15}$$

$$kt = \ln [CH_3CH_2Cl]_0 - \ln [CH_3CH_2Cl]_t = \ln \frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t} \tag{14.5.16}$$

$$t = \frac{1}{k}\left(\ln \frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}\right) = \frac{1}{1.6 \times 10^{-6}\ \text{s}^{-1}}\left(\ln \frac{0.0200\ \text{M}}{0.0050\ \text{M}}\right) \tag{14.5.17}$$

$$= \frac{\ln 4.0}{1.6 \times 10^{-6}\ \text{s}^{-1}} = 8.7 \times 10^5\ \text{s} = 240\ \text{h} = 2.4 \times 10^2\ \text{h} \tag{14.5.18}$$

Exercise 14.5.2

In the exercise above, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C. 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. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer 0.0252 M; 29 h

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Example Using the First-Order Integrated Rate Law Equation:

https://youtu.be/fLY6MtNl9-g

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14.6: 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 2A → products. 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:

$$\text{rate} = -\frac{\Delta[\text{A}]}{2\Delta t} = k[\text{A}]^2 \tag{14.6.1}$$

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:

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt \tag{14.6.2}$$

Because Equation 14.6.2 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[\text{A}]$ and $b = 1/[\text{A}]_0$, 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 $1/[\text{A}]_0$.

Note

Second-order reactions generally have the form 2A → products or A + B → products.

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:

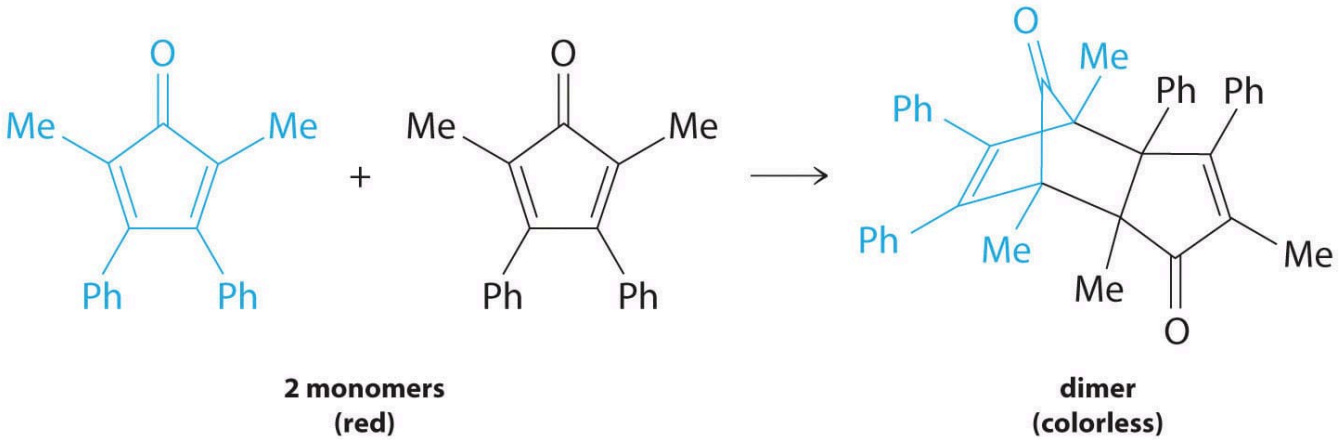


Figure 14.6.1

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 14.6.1) or the integrated rate law (Equation 14.6.2).

Table 14.6.1: 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 14.6.1. 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:

$$\frac{5.0 \times 10^{-5}\ \text{M/min}}{1.8 \times 10^{-5}\ \text{M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3}\ \text{M}}{2.0 \times 10^{-3}\ \text{M}} = 1.7 \tag{14.6.3}$$

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 14.6.1 and the data from any row in Table 14.6.1, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \tag{14.6.4}$$

$$8.0 \times 10^{-5}\ \text{M/min} = k(4.4 \times 10^{-3}\ \text{M})^2 \tag{14.6.5}$$

$$4.1\ \text{M}^{-1} \cdot \text{min}^{-1} = k \tag{14.6.6}$$

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 part (a) in Figure 14.6.2. 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 part (b) in Figure 14.6.7. 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.

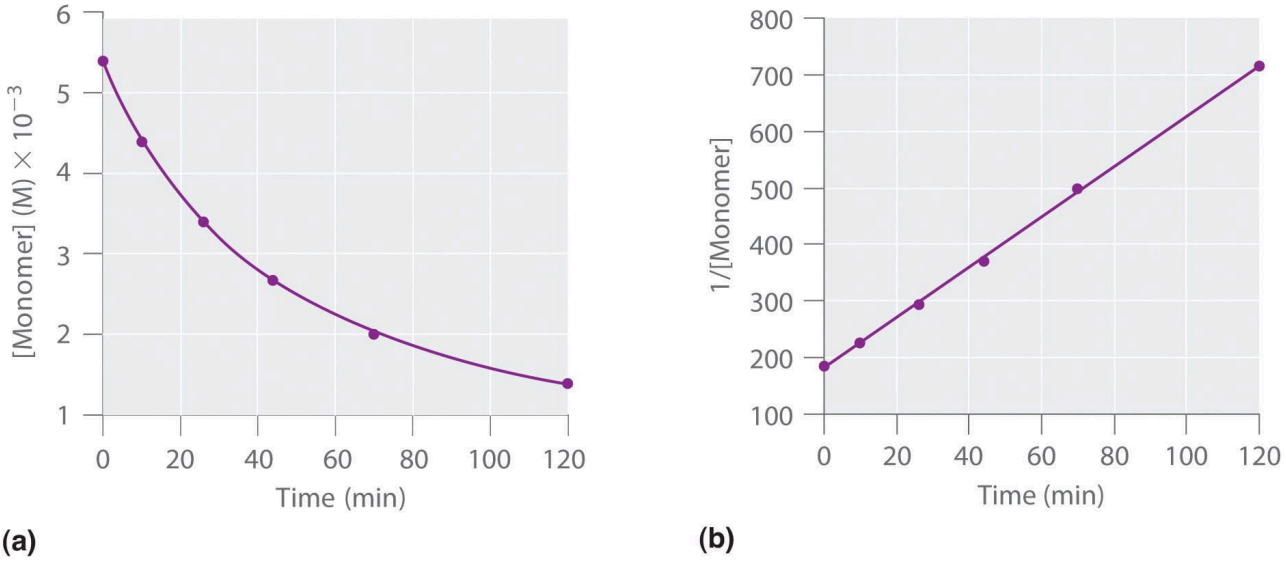


Figure 14.6.2: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.6.6 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple 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 14.6.1

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2NO_2(g) \xrightarrow{\Delta} 2NO(g) + O_2(g) \tag{14.6.7}$$

Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

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:

$$\text{rate} = k[\text{NO}_2]^2 \tag{14.6.8}$$

$$5.40 \times 10^{-5}\ \text{M/s} = k(0.010\ \text{M})^2 \tag{14.6.9}$$

$$0.54\ \text{M}^{-1} \cdot \text{s}^{-1} = k \tag{14.6.10}$$

Exercise 14.6.1

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:

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 second order in HO_2; $k = 1.4 \times 10^9\ M^{-1} \cdot s^{-1}$

Note

If a plot of reactant concentration versus time is **not** linear, but a plot of 1/reaction concentration versus time is linear, then the reaction is second order.

Example 14.6.2

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 14.6.2) 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,

$$\frac{1}{[NO_2]_{3600}} = \frac{1}{[NO_2]_0} + kt = \frac{1}{0.056\ \text{M}} + [(0.54\ \text{M}^{-1}\cdot\text{s}^{-1})(3600\ \text{s})] \tag{14.6.11}$$

$$= 2.0 \times 10^3\ \text{M}^{-1} \tag{14.6.12}$$

Thus $[NO_2]_{3600}$ = 5.1 × 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 14.6.2 for t, using the concentrations given.

$$t = \frac{(1/[NO_2]) - (1/[NO_2]_0)}{k} = \frac{(1/0.0056\ \text{M}) - (1/0.056\ \text{M})}{0.54\ \text{M}^{-1}\cdot\text{s}^{-1}} = 3.0 \times 10^2\ \text{s} = 5.0\ \text{min}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Exercise 14.6.2

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as k = 1.4 × 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 14.6.2) and the rate constant calculated in the exercise in Example 14.6.3.

Answer 2.0 × 10^{-13} M; 6.4 × 10^{-6} s

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:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t} = k[\text{A}][\text{B}] \tag{14.6.13}$$

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.

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14.7: Reaction Kinetics: A Summary

Learning Objectives

- To use graphs to analyze the kinetics of a reaction.

You learned that the integrated rate law for each common type of reaction (zeroth, first, or second order in a single reactant) can be plotted as a straight line. Using these plots offers an alternative to the methods described for showing how reactant concentration changes with time and determining reaction order.

We will illustrate the use of these graphs by considering the thermal decomposition of NO_2 gas at elevated temperatures, which occurs according to the following reaction:

$$(2NO_2(g) \xrightarrow{\Delta} 2NO(g) + O_2(g) \tag{14.7.1}$$

Experimental data for this reaction at 330°C are listed in Table 14.7.1; they are provided as [NO_2], ln[NO_2], and 1/[NO_2] versus time to correspond to the integrated rate laws for zeroth-, first-, and second-order reactions, respectively. The actual concentrations of NO_2 are plotted versus time in part (a) in Figure 14.7.1.

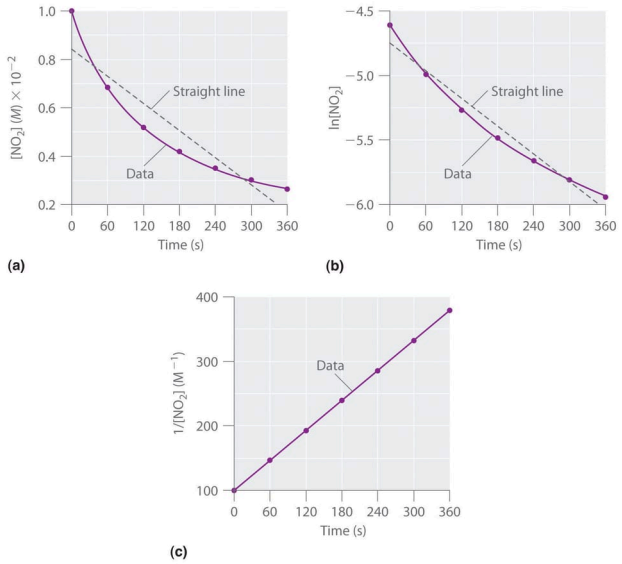


Figure 14.7.1: The Decomposition of NO_2. These plots show the decomposition of a sample of NO_2 at 330°C as (a) the concentration of NO_2 versus t, (b) the natural logarithm of [NO_2] versus t, and (c) 1/[NO_2] versus t.

Because the plot of [NO_2] versus *t* is not a straight line, we know the reaction is not zeroth order in NO_2. A plot of ln[NO_2] versus *t* (part (b) in Figure 14.7.1) shows us that the reaction is not first order in NO_2 because a first-order reaction would give a straight line. Having eliminated zeroth-order and first-order behavior, we construct a plot of 1/[NO_2] versus *t* (part (c) in Figure 14.7.1). This plot is a straight line, indicating that the reaction is second order in NO_2.

Table 14.7.1: Concentration of NO_2 as a Function of Time at 330°C

Time (s)	[NO_2] (M)	ln[NO_2]	1/[NO_2] (M^{-1})
0	1.00×10^{-2}	−4.605	100
60	6.83×10^{-3}	−4.986	146
120	5.18×10^{-3}	−5.263	193

Time (s)	$[NO_2]$ (M)	$\ln[NO_2]$	$1/[NO_2]$ (M^{-1})
180	4.18×10^{-3}	−5.477	239
240	3.50×10^{-3}	−5.655	286
300	3.01×10^{-3}	−5.806	332
360	2.64×10^{-3}	−5.937	379

We have just determined the reaction order using data from a single experiment by plotting the concentration of the reactant as a function of time. Because of the characteristic shapes of the lines shown in Figure 14.7.2, the graphs can be used to determine the reaction order of an unknown reaction. In contrast, the method of initial rates required multiple experiments at different NO_2 concentrations as well as accurate initial rates of reaction, which can be difficult to obtain for rapid reactions.

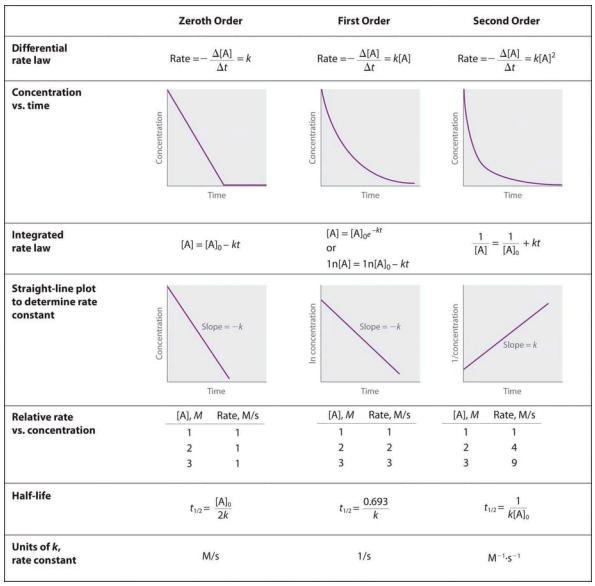


Figure 14.7.2: Properties of Reactions That Obey Zeroth-, First-, and Second-Order Rate Laws

Example 14.7.1

Dinitrogen pentoxide (N_2O_5) decomposes to NO_2 and O_2 at relatively low temperatures in the following reaction:

$$2N_2O_5(soln) \rightarrow 4NO_2(soln) + O_2(g)$$

This reaction is carried out in a CCl_4 solution at 45°C. The concentrations of N_2O_5 as a function of time are listed in the following table, together with the natural logarithms and reciprocal N_2O_5 concentrations. Plot a graph of the concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t* and then determine the rate law and calculate the rate constant.

Time (s)	$[N_2O_5]$ (M)	$\ln[N_2O_5]$	$1/[N_2O_5]$ (M^{-1})
0	0.0365	−3.310	27.4
600	0.0274	−3.597	36.5
1200	0.0206	−3.882	48.5
1800	0.0157	−4.154	63.7
2400	0.0117	−4.448	85.5

3000	0.00860	−4.756	116
3600	0.00640	−5.051	156

Given: balanced chemical equation, reaction times, and concentrations

Asked for: graph of data, rate law, and rate constant

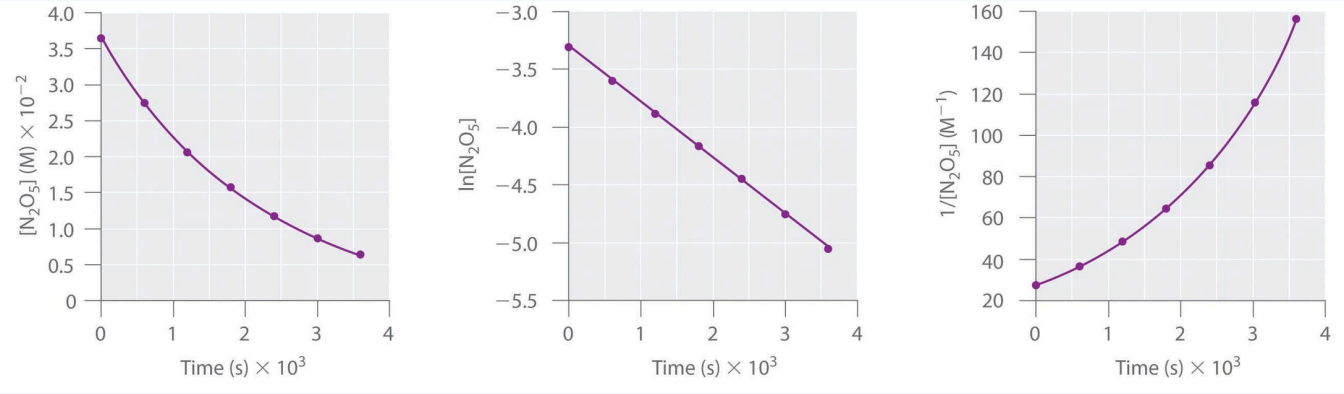
Strategy:

A Use the data in the table to separately plot concentration, the natural logarithm of the concentration, and the reciprocal of the concentration (the vertical axis) versus time (the horizontal axis). Compare the graphs with those in Figure 14.7.1 to determine the reaction order.

B Write the rate law for the reaction. Using the appropriate data from the table and the linear graph corresponding to the rate law for the reaction, calculate the slope of the plotted line to obtain the rate constant for the reaction.

Solution

A Here are plots of $[N_2O_5]$ versus t, $\ln[N_2O_5]$ versus t, and $1/[N_2O_5]$ versus t:



The plot of $\ln[N_2O_5]$ versus t gives a straight line, whereas the plots of $[N_2O_5]$ versus t and $1/[N_2O_5]$ versus t do not. This means that the decomposition of N_2O_5 is first order in $[N_2O_5]$.

B The rate law for the reaction is therefore

$$\text{rate} = k[N_2O_5]$$

Calculating the rate constant is straightforward because we know that the slope of the plot of ln[A] versus t for a first-order reaction is $-k$. We can calculate the slope using any two points that lie on the line in the plot of $\ln[N_2O_5]$ versus t. Using the points for t = 0 and 3000 s,

$$\text{slope} = \frac{\ln[N_2O_5]_{3000} - \ln[N_2O_5]_0}{3000\ \text{s} - 0\ \text{s}} = \frac{(-4.756) - (-3.310)}{3000\ \text{s}} = -4.820 \times 10^{-4}\ \text{s}^{-1} \tag{14.7.2}$$

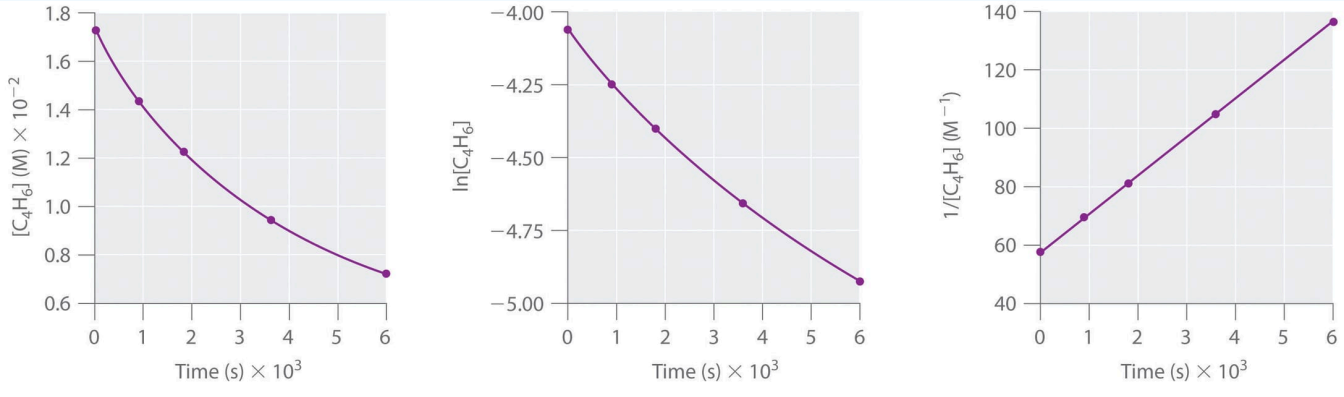
Thus $k = 4.820 \times 10^{-4}\ \text{s}^{-1}$.

Exercise 14.7.1

1,3-Butadiene (CH_2=CH—CH=CH_2; C_4H_6) is a volatile and reactive organic molecule used in the production of rubber. Above room temperature, it reacts slowly to form products. Concentrations of C_4H_6 as a function of time at 326°C are listed in the following table along with ln[C_4H_6] and the reciprocal concentrations. Graph the data as concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t*. Then determine the reaction order in C_4H_6, the rate law, and the rate constant for the reaction.

Time (s)	[C_4H_6] (M)	ln[C_4H_6]	1/[C_4H_6] (M^{-1})
0	1.72×10^{-2}	−4.063	58.1
900	1.43×10^{-2}	−4.247	69.9
1800	1.23×10^{-2}	−4.398	81.3
3600	9.52×10^{-3}	−4.654	105
6000	7.30×10^{-3}	−4.920	137

Answer



second order in C_4H_6; rate = $k[C_4H_6]^2$; $k = 1.3 \times 10^{-2}\ M^{-1}{\cdot}s^{-1}$

Summary

For a zeroth-order reaction, a plot of the concentration of any reactant versus time is a straight line with a slope of –*k*. For a first-order reaction, a plot of the natural logarithm of the concentration of a reactant versus time is a straight line with a slope of –*k*. For a second-order reaction, a plot of the inverse of the concentration of a reactant versus time is a straight line with a slope of *k*.

Key Takeaway

- Plotting the concentration of a reactant as a function of time produces a graph with a characteristic shape that can be used to identify the reaction order in that reactant.

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14.8: Theoretical Models for Chemical Kinetics

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14.9: The Effect of Temperature on Reaction Rates

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:

$$Z_{AB} = N_A N_B \left(r_A + r_B\right)^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}} \tag{14.9.1}$$

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 14.9.1 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 $14.9.1$ 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.

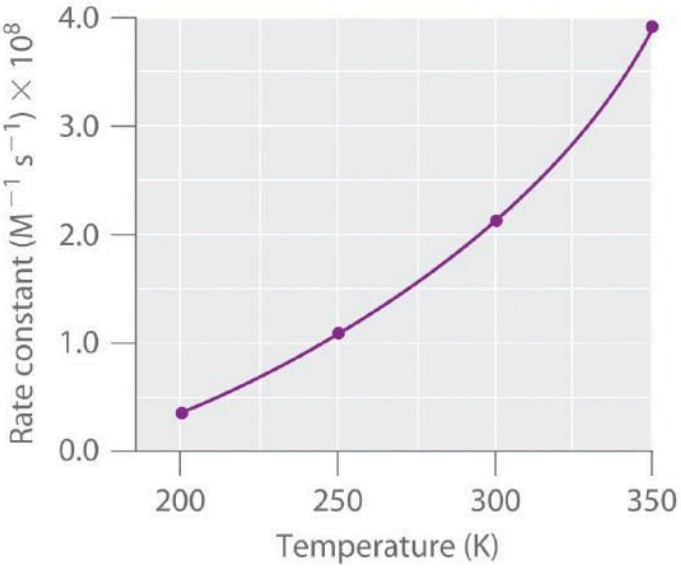


Figure $14.9.1$: Rate Constant versus Temperature for the Reaction of NO with $\mathrm{O_3}$The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature 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 $14.9.2$ 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.

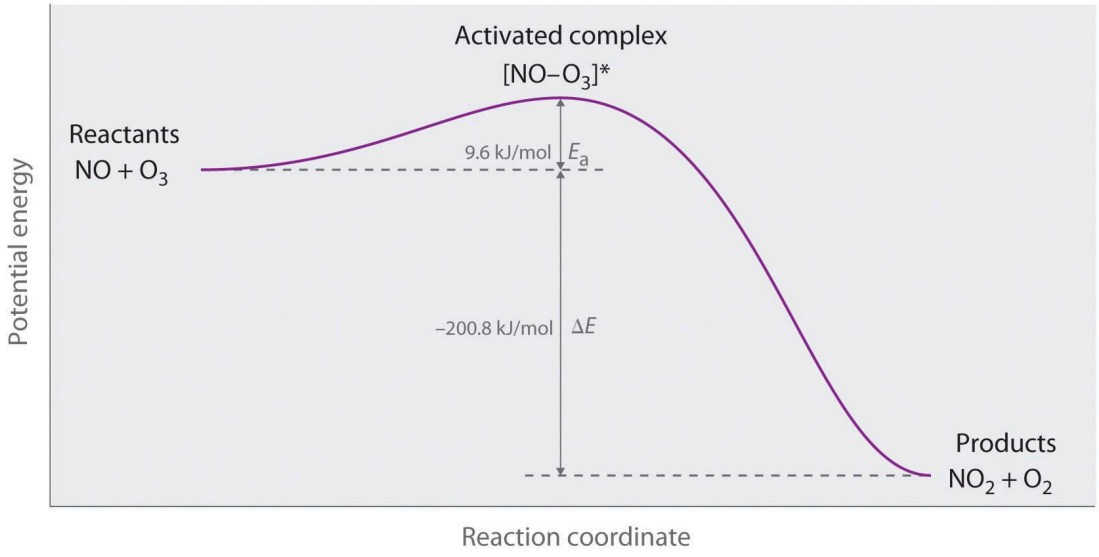


Figure $14.9.2$: Energy of the Activated Complex for the $NO–O_3$ System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex. (CC BY-SA-NC; anonymous)

Figure $14.9.3a$ illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, Figure $14.9.3b$ 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.

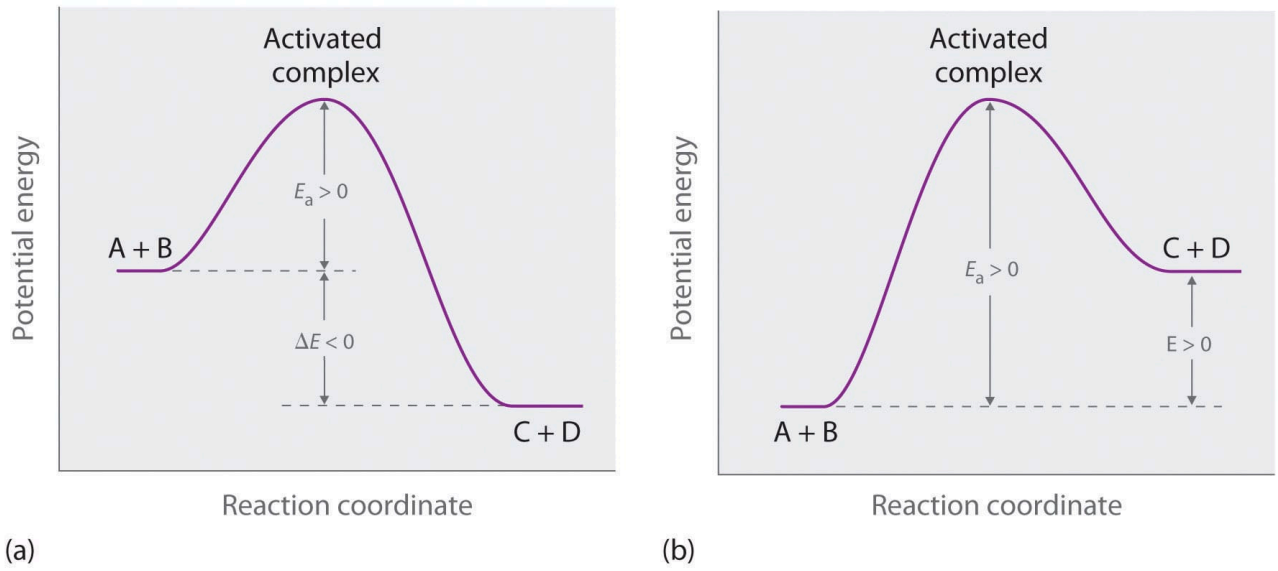


Figure 14.9.3: Differentiating between E_a and ΔE. The potential energy diagrams for a reaction with (a) ΔE < 0 and (b) ΔE > 0 illustrate the change in the potential energy of the system as reactants are converted to products. In both cases, E_a is positive. For a reaction such as the one shown in (b), 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 14.9.4 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.

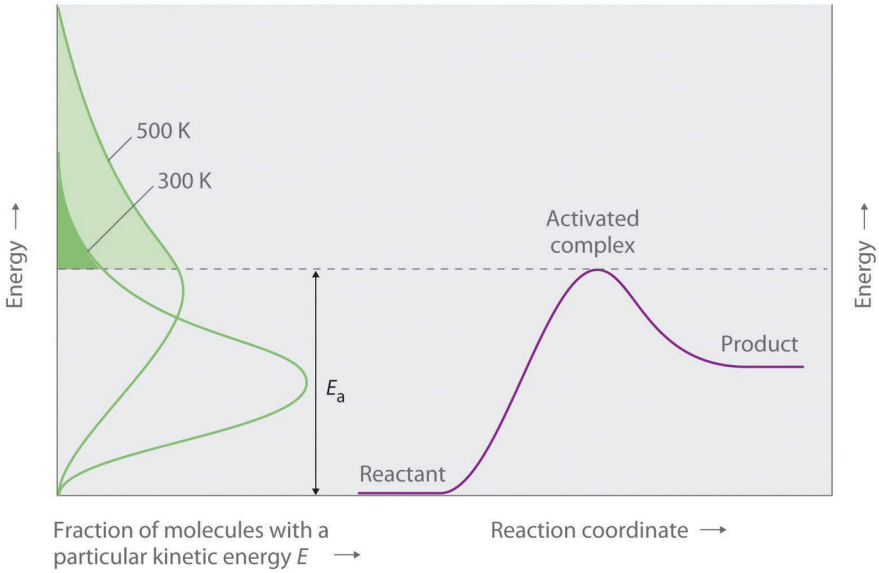


Figure 14.9.4: Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution 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 14.9.4). 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).

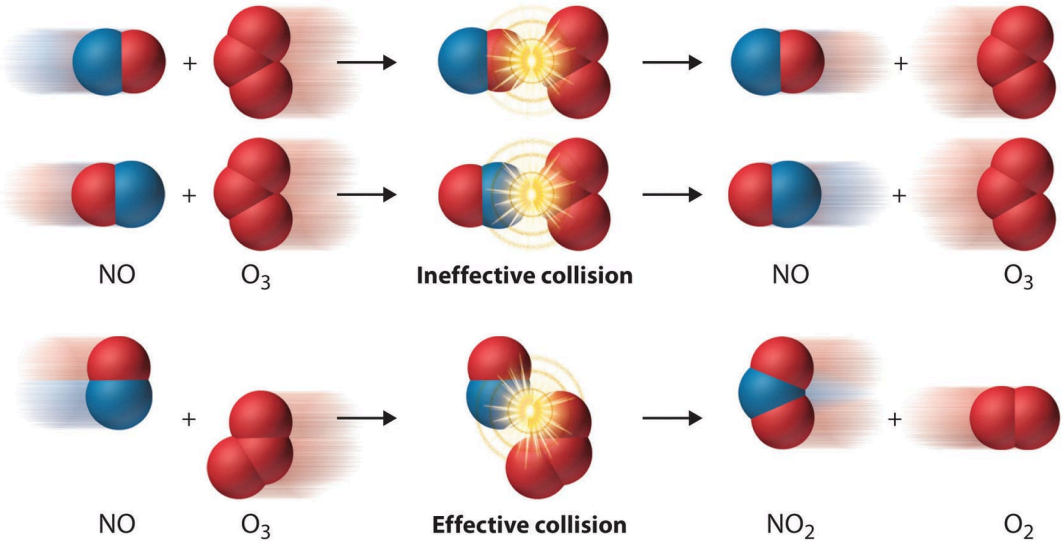


Figure 14.9.4: The Effect of Molecular Orientation on the Reaction of NO and $\mathrm{O_3}$. Most collisions of NO and $\mathrm{O_3}$ molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of $\mathrm{O_3}$ 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

$$\text{rate} = k[A][B] \tag{14.9.2}$$

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**:

$$k = Ae^{-E_a/RT} \tag{14.9.3}$$

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 14.9.1). 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 14.9.3 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 14.9.3,

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right) \tag{14.9.4}$$

$$= \ln A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right] \tag{14.9.5}$$

Equation 14.9.5 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 14.9.1.

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A Video Discussing The Arrhenius Equation: The Arrhenius Equation(opens in new window) [youtu.be]

Example 14.9.1: 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 14.9.5 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 14.9.6).

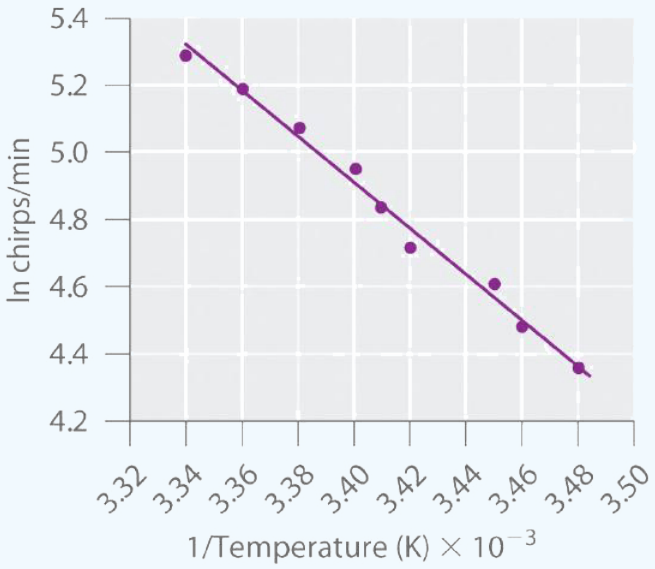


Figure 14.9.6: Graphical Determination of E_a for Tree Cricket Chirping. When the natural logarithm of the rate of tree cricket chirping is plotted versus 1/T, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an E_a of 55 kJ/mol. (CC 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 14.9.6 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 14.9.5 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 14.9.1A

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 $14.9.1B$

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 $14.9.1A$

E_a = 114 kJ/mol; k_{700}= 18,600 $M^{-1}{\cdot}s^{-1}$ = 1.86 × 10^4 $M^{-1}{\cdot}s^{-1}$.

Exercise $14.9.1B$

about 51 kJ/mol

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14.10: 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:

$$2\,C_8H_{18}\,(l) + 25\,O_2\,(g) \longrightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g) \tag{14.10.1}$$

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.

$$NO_2\,(g) + CO\,(g) \longrightarrow NO\,(g) + CO_2\,(g) \tag{14.10.2}$$

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:

$$rate = k[{NO_2}^2] \tag{14.10.3}$$

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!)

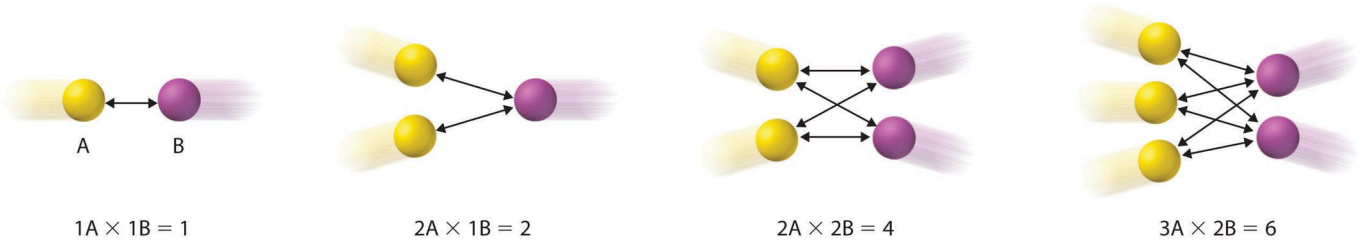


Figure 14.10.1: The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases 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 14.10.1). 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 14.10.1. For a bimolecular elementary reaction of the form A + B → products, the general rate law is

$$rate = k[A][B].$$

Table 14.10.1: 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	$\mathrm{NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO}$	$\mathrm{rate} = k_1[\mathrm{NO_2}]^2 \ \mathrm{(predicted)}$
step 2	$\underline{\mathrm{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}}$	$\mathrm{rate} = k_2[\mathrm{NO_3}][\mathrm{CO}] \ \mathrm{(predicted)}$
sum	$\mathrm{NO_2 + CO \xrightarrow{k} NO + CO_2}$	$\mathrm{rate} = k[\mathrm{NO_2}]^2 \ \mathrm{(observed)}$

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 14.10.1: 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 14.10.1

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 14.10.2 : 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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14.11: 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 14.11.1). 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.

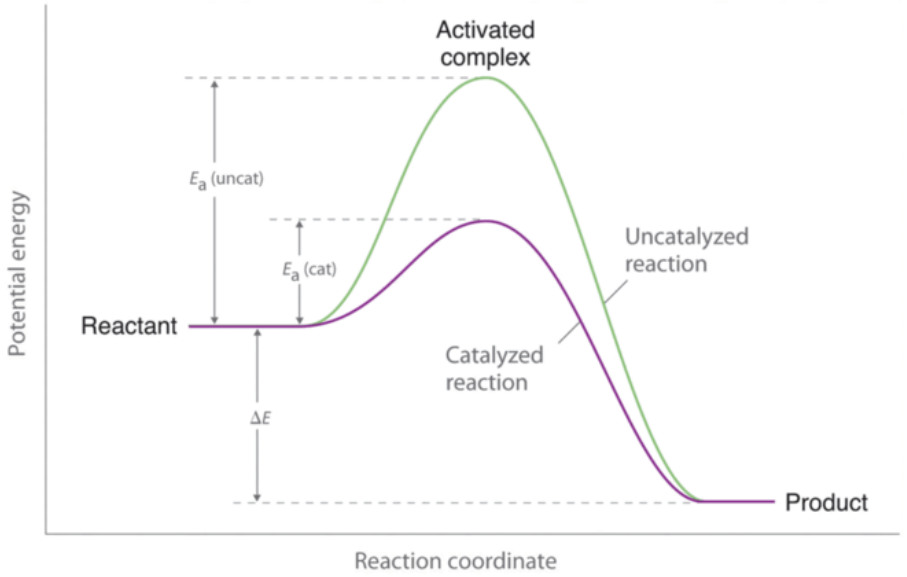


Figure 14.11.1: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect 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 .

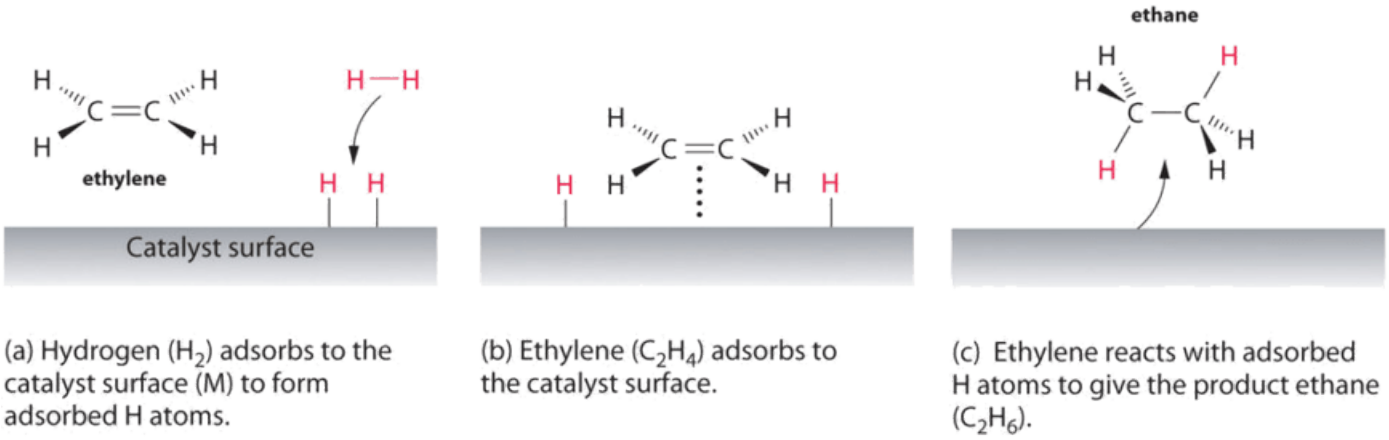
A catalyst affects E_a, not ΔE.

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 14.11.2, 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 14.11.2: 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 14.11.2 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 14.11.1. 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 14.11.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

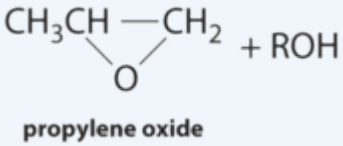
Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	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 14.11.2), 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 14.11.2: 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 14.11.3).



Figure 14.11.3: 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

14.7: Reaction Kinetics: A Summary

Conceptual Problems

1. Compare first-order differential and integrated rate laws with respect to the following. Is there any information that can be obtained from the integrated rate law that cannot be obtained from the differential rate law?

    a. the magnitude of the rate constant
    b. the information needed to determine the order
    c. the shape of the graphs

2. In the single-step, second-order reaction 2A → products, how would a graph of [A] versus time compare to a plot of 1/[A] versus time? Which of these would be the most similar to the same set of graphs for A during the single-step, second-order reaction A + B → products? Explain.

3. For reactions of the same order, what is the relationship between the magnitude of the rate constant and the reaction rate? If you were comparing reactions with different orders, could the same arguments be made? Why?

Answers

1.

    a. For a given reaction under particular conditions, the magnitude of the first-order rate constant does not depend on whether a differential rate law or an integrated rate law is used.
    b. The differential rate law requires multiple experiments to determine reactant order; the integrated rate law needs only one experiment.
    c. Using the differential rate law, a graph of concentration versus time is a curve with a slope that becomes less negative with time, whereas for the integrated rate law, a graph of ln[reactant] versus time gives a straight line with slope = $-k$. The integrated rate law allows you to calculate the concentration of a reactant at any time during the reaction; the differential rate law does not.

3. The reaction rate increases as the rate constant increases. We cannot directly compare reaction rates and rate constants for reactions of different orders because they are not mathematically equivalent.

Numerical Problems

1. One method of using graphs to determine reaction order is to use relative rate information. Plotting the log of the relative rate versus log of relative concentration provides information about the reaction. Here is an example of data from a zeroth-order reaction:

Relative [A] (M)	Relative Rate (M/s)
1	1
2	1
3	1

    Varying [A] does not alter the reaction rate. Using the relative rates in the table, generate plots of log(rate) versus log(concentration) for zeroth-, first- and second-order reactions. What does the slope of each line represent?

2. The table below follows the decomposition of N_2O_5 gas by examining the partial pressure of the gas as a function of time at 45°C. What is the reaction order? What is the rate constant? How long would it take for the pressure to reach 105 mmHg at

45°C?

Time (s)	Pressure (mmHg)
0	348
400	276
1600	156
3200	69
4800	33

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15: PRINCIPLES OF CHEMICAL EQUILIBRIUM

Petrucci: *General Chemistry*
Principles and Modern Applications

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15.3: Relationships Involving Equilibrium Constants
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15.6: Altering Equilibrium Conditions - Le Châtelier's Principle
15.7: Equilibrium Calculations - Some Illustrative Examples

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15.1: Dynamic 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.

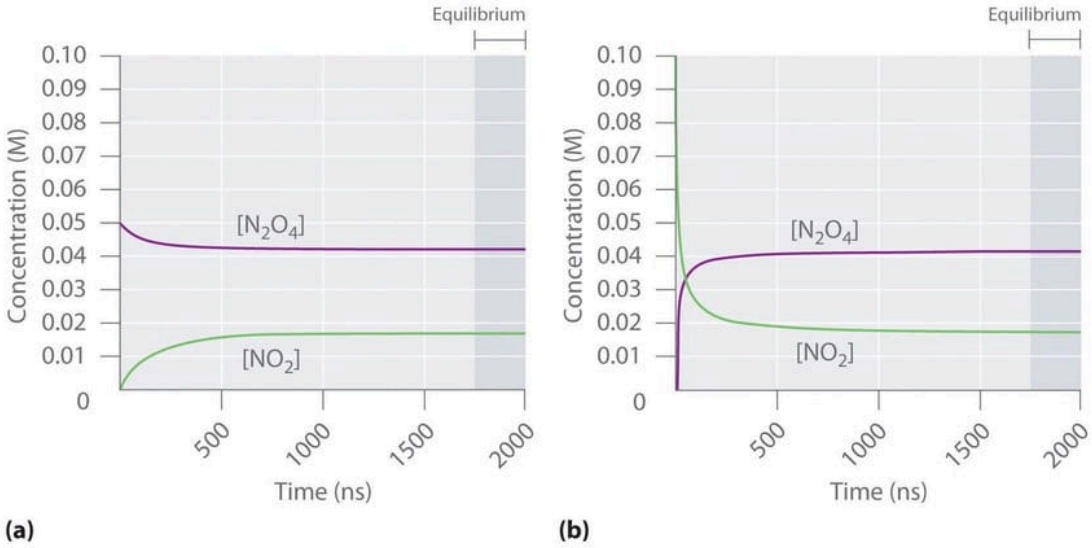


Figure 15.1.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system 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.

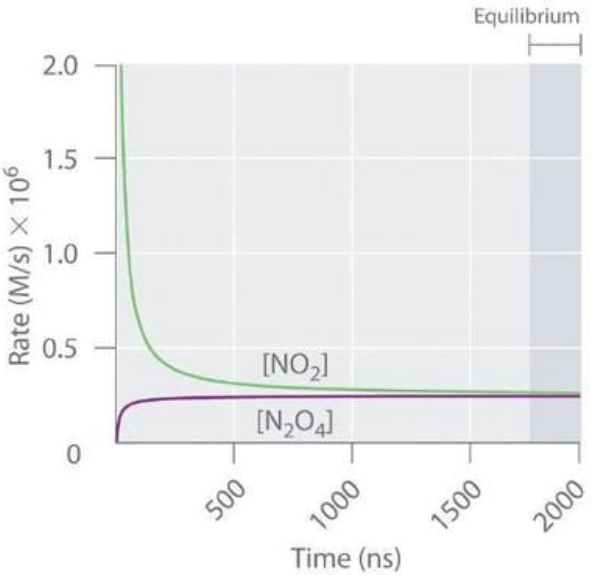


Figure 15.1.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \diamondsuit 2NO_{2(g)}$ System Shown in Part (b) in Figure 15.1.2. (CC BY-SA-NC; Anonymous by request)

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.

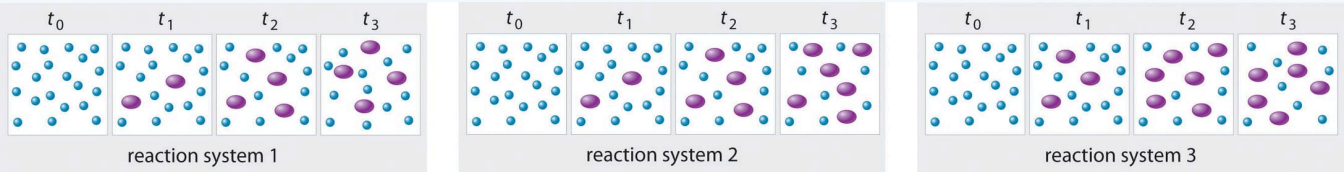
At equilibrium, the forward reaction rate is equal to the reverse reaction rate.

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:

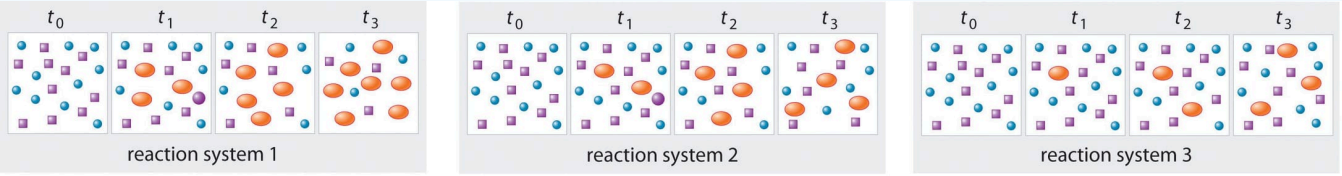
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

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 Expression

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 system described in Equation 15.2.1, the decomposition of N_2O_4 to NO_2. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_4] \tag{15.2.1}$$

and

$$\text{reverse rate} = k_r[NO_2]^2 \tag{15.2.2}$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[N_2O_4] = k_r[NO_2]^2 \tag{15.2.3}$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \tag{15.2.4}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{15.2.5}$$

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.

Table 15.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation ???. At equilibrium the magnitude of the quantity $[NO_2]^2/[N_2O_4]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of NO_2 and N_2O_4 are, at equilibrium the quantity $[NO_2]^2/[N_2O_4]$ 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}

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
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}

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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

$$aA + bB \rightleftharpoons cC + dD \tag{15.2.6}$$

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 and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.2.7}$$

where K is the equilibrium constant for the reaction. Equation 15.2.6 is called the equilibrium equation, and the right side of Equation 15.2.7 is called the equilibrium constant expression. The relationship shown in Equation 15.2.7 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)
$\mathrm{S(s) + O_2(g) \rightleftharpoons SO_2(g)}$	300	4.4×10^{53}
$\mathrm{2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)}$	500	2.4×10^{47}

***Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.**

Reaction	Temperature (K)	Equilibrium Constant (K)
$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$	300	1.6×10^{33}
$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$	300	4.1×10^{18}
$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$	300	4.2×10^{13}
$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$	300	2.7×10^{8}
$H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)$	100	1.92
$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$	300	2.9×10^{-1}
$I_2(g) \rightleftharpoons 2\,I(g)$	800	$4.6 \times ^{10-7}$
$Br_2(g) \rightleftharpoons 2\,Br(g)$	1000	4.0×10^{-7}
$Cl_2(g) \rightleftharpoons 2\,Cl(g)$	1000	1.8×10^{-9}
$F_2(g) \rightleftharpoons 2\,F(g)$	500	7.4×10^{-13}
***Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.**		

You will also notice in Table 15.2.2 that equilibrium constants have no units, even though Equation 15.2.7 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 15.2.8, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{15.2.8}$$

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:

$$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)} \tag{15.2.9}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{15.2.10}$$

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

$$\text{reactants} \rightleftharpoons \text{products}. \tag{15.2.11}$$

Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 15.2.8 and 15.2.7), 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.

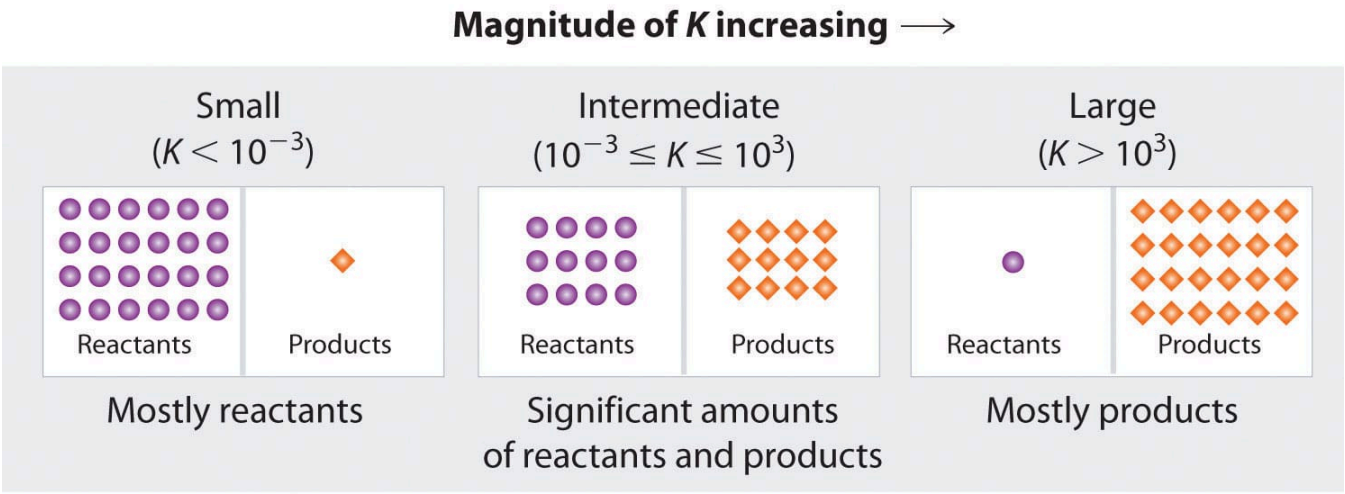


Figure 15.2.3: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

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

Write the equilibrium constant expression for each reaction.

- $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$
- $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 15.2.7. 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, N_2 has a coefficient of 1 and H2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} \tag{15.2.12}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}} \tag{15.2.13}$$

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:

$$\frac{[CO]^2[O_2]}{[CO_2]^2} \tag{15.2.14}$$

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. $2C_8H_{18(g)} + 25O_{2(g)} \rightleftharpoons 16CO_{2(g)} + 18H_2O_{(g)}$
c. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Answer:

a. $K = \dfrac{[N_2][O_2]^{1/2}}{[N_2O]}$
b. $K = \dfrac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$
c. $K = \dfrac{[HI]^2}{[H_2][I_2]}$

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.

a. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
b. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
c. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
d. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

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:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{15.2.15}$$

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
- $K_{327°C} = 4.1$.

At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?

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. 327°C, where K is smallest
b. 25°C

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 15.2.6 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{15.2.16}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{15.2.17}$$

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 N_2O_4 \rightleftharpoons 2NO_2\) is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{15.2.18}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{15.2.19}$$

Consider another example, the formation of water: $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. Because H_2 is a good reductant and 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 O_2 and 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 H_2 and 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

$$2NO_2 \rightleftharpoons N_2O_4 \tag{15.2.20}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{15.2.21}$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{15.2.22}$$

The values for K′ (Equation 15.2.19) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{15.2.23}$$

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.

Example 15.2.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$$

What is the equilibrium constant for each related reaction at 745 K?

a. $2NH_{3(g)} \rightleftharpoons N2(g) + 3H_{2(g)}$
b. $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$

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:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118 \tag{15.2.24}$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47 \tag{15.2.25}$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344 \tag{15.2.26}$$

Exercise 15.2.3

At 527°C, the equilibrium constant for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \tag{15.2.27}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)} \tag{15.2.28}$$

Answer: 3.6×10^{-3}

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Determining the Equilibrium Expression: https://youtu.be/ZK9cMIWFerY

Summary

- 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:

$$K_p = K(RT)^{\Delta n}$$

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.

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15.3: Relationships Involving Equilibrium Constants

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To understand how different phases affect equilibria.

Relating Stoichiometry and Equilibrium Constants

It is important to remember that an equilibrium constant is always tied to a specific chemical equation, and if we write the equation in reverse or multiply its coefficients by a common factor, the value of K will change. Fortunately, the rules are very simple:

- Writing the equation in **reverse** will invert the equilibrium expression and
- **Multiplying** the coefficients by a common factor will raise *K* to the corresponding power.

Here are some of the possibilities for the reaction involving the equilibrium between gaseous water and its elements:

$2H_2 + O_2 \rightleftharpoons 2H_2O$	$10H_2 + 5O_2 \rightleftharpoons 10H_2O$	$H_2 + ½O_2 \rightleftharpoons H_2O$	$H_2O \rightleftharpoons H_2 + ½O_2$
$K_p = \dfrac{P^2_{H_2O}}{P^2_{H_2}P_{O_2}}$	$K_p = \dfrac{P^{10}_{H_2O}}{P^{10}_{H_2}P^5_{O_2}} = \left(\dfrac{P^2_{H_2O}}{P^2_{H_2}P_{O_2}}\right)^5$	$K_p = \dfrac{P_{H_2O}}{P_{H_2}P^{1/2}_{O_2}} = \left(\dfrac{P^2_{H_2O}}{P^2_{H_2}P_{O_2}}\right)^{1/2}$	$K_p = \dfrac{P_{H_2}P^{1/2}_{O_2}}{P_{H_2O}} = \left(\dfrac{P^2_{H_2O}}{P^2_{H_2}P_{O_2}}\right)^{-1/2}$

Many chemical changes can be regarded as the sum or difference of two or more other reactions. If we know the equilibrium constants of the individual processes, we can easily calculate that for the overall reaction according to the following rule:

The Multi-step Equilibrium Rule

The equilibrium constant for the **sum** of two or more reactions is the **product** of the equilibrium constants for each of the steps.

Example 15.3.1

Calculate the value of K for the reaction

$$CaCO_{3(s)} + H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + HCO^-_{3(aq)} \tag{15.3.1}$$

given the following equilibrium constants:

$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$	$K_1 = 10^{-6.3}$

$HCO_{3(aq)}^{-} \rightleftharpoons H_{(aq)}^{+} + CO_{3(aq)}^{2-}$	$K_2 = 10^{-10.3}$

Solution

The net reaction is the sum of reaction 1 and the reverse of reaction 2:

$CaCO_{3(s)} \rightleftharpoons Ca_{(aq)}^{2+} + CO_{3(aq)}^{2-}$	$K_1 = 10^{-6.3}$
$H_{(aq)}^{+} + CO_{3(aq)}^{2-} \rightleftharpoons HCO_{3(aq)}^{-}$	$K_{-2} = 10^{-(-10.3)}$
$CaCO_{3(s)} + H_{(aq)}^{+} \rightarrow Ca_{(aq)}^{2+} + HCO_{3(aq)}^{-}$	$K = \frac{K_1}{K_2} = 10^{(-6.3+10.3)} = 10^{+4.0}$

Comment:

This net reaction describes the dissolution of limestone by acid; it is responsible for the eroding effect of acid rain on buildings and statues. This an example of a reaction that has practically no tendency to take place by itself (small K_1) being "driven" by a second reaction having a large equilibrium constant (K_{-2}). From the standpoint of the Le Chatelier principle, the first reaction is "pulled to the right" by the removal of carbonate by hydrogen ion. *Coupled* reactions of this type are widely encountered in all areas of chemistry, and especially in biochemistry, in which a dozen or so reactions may be linked.

Example 15.3.2

The synthesis of HBr from hydrogen and liquid bromine has an equilibrium constant $K_p = 4.5 \times 10^{15}$ at 25°C. Given that the vapor pressure of liquid bromine is 0.28 atm, find K_p for the homogeneous gas-phase reaction at the same temperature.

Solution

The net reaction we seek is the sum of the heterogeneous synthesis of HBr and the *reverse* of the vaporization of liquid bromine:

$H_{2(g)} + Br_{2(l)} \rightleftharpoons 2HBr_{(g)}$	$K_p = 4.5 \times 10^{15}$
$Br_{2(g)} \rightleftharpoons Br_{2(l)}$	$K_p = (0.28)^{-1}$
$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$	$K_p = 1.6 \times 10^{19}$

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Relationships Involving Equilibrium Constants: https://youtu.be/2vZDpXX1zr0

Equilibria Involving 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):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{15.3.2}$$

Thus K_p for the decomposition of N_2O_4 is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{15.3.3}$$

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):

$$K_p = K_c(RT)^{\Delta n} \tag{15.3.4}$$

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 15.3.3, $K_p = K$ 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,

$$K_p = K(RT)^1 = K_cRT \tag{15.3.5}$$

Example 15.3.4: The Haber Process

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:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{15.3.6}$$

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 15.3.3 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 15.2.15, we have the following:

$$K_p = K(RT)^{-2} = \frac{K}{(RT)^2} = \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} = 3.16 \times 10^{-5} \tag{15.3.7}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise 15.3.4

Calculate K_p for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \tag{15.3.8}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer: $K_p = 1.2 \times 10^3$

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Converting Kc to Kp: https://youtu.be/_2WVnlqXrV4

Combining Equilibrium Constant Expressions

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 N_2 with O_2 to give NO_2. This reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (2). The equilibrium constant for each reaction at 1000°C is also given.

1. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad K_1 = 2.0 \times 10^{-25}$
2. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_2 = 6.4 \times 10^9$

Summing reactions (1) and (2) gives the overall reaction of N_2 with O_2:

3. $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_3 = ?$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2} \tag{15.3.9}$$

What is the relationship between K_1, K_2, and K_3, all at 1000°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,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}\,[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3 \tag{15.3.10}$$

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:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15} \tag{15.3.11}$$

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 15.3.2

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:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)} \tag{15.3.12}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)} \tag{15.3.13}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \tag{15.3.14}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^{4}) = 3.03 \times 10^{3} \tag{15.3.15}$$

Exercise 15.3.2

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. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \qquad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_3 = ?$

Answer: $K_3 = 1.1 \times 10^{66}$

Heterogeneous 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.

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids.The reference states for pure solids and liquids are those forms stable at 1 bar (approximately 1 atm), which are assigned an **activity of 1**. (Recall that the density of water, and thus its volume, changes by only a few percentage points between 0°C and 100°C.)

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)} \tag{15.3.16}$$

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:

$$K = \frac{[CO]^2}{[CO_2][C]} \tag{15.3.17}$$

Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:

$$[C] = \frac{2.26 \cancel{g/cm^3}}{12.01 \cancel{g/mol}} \times 1000 \cancel{cm^3}/L = 188\ mol/L = 188\ M \tag{15.3.18}$$

We can rearrange Equation 15.3.8 so that the constant terms are on one side:

$$K[C] = K(188) = \frac{[CO]^2}{[CO_2]} \tag{15.3.19}$$

Incorporating the constant value of $[C]$ into the equilibrium equation for the reaction in Equation 15.3.7,

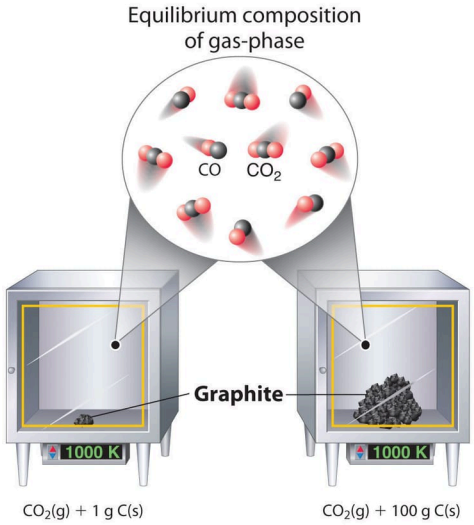
$$K' = \frac{[CO]^2}{[CO_2]} \tag{15.3.20}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{15.3.21}$$

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 concentrations 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 CO_2, the system described in Equation 15.3.7 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 15.3.1, 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 15.3.1: 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 15.3.3

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)}$
b. $Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(g)}$

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 concentrations do not appear in the equilibrium constant expression because they do not change significantly. So

$$K = \frac{1}{[Cl_2]} \tag{15.3.22}$$

and

$$K_p = \frac{1}{P_{Cl_2}} \tag{15.3.23}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

$$K = \frac{[H_2O]^4}{[H_2]^4} \tag{15.3.24}$$

and

$$K_p = \frac{(P_{H_2O})^4}{(P_{H_2})^4} \tag{15.3.25}$$

Exercise 15.3.3

Write the expressions for K and K_p for the following reactions.

a. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
b. $\underset{glucose}{C_6H_{12}O_{6(s)}} + 6O_{2(g)} \rightleftharpoons 6CO_{2(g)} + 6H_2O_{(g)}$

Answer:

a. $K = [CO_2]$ and $K_p = P_{CO_2}$
b. $K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that pure water is about 55.5 M, and pure ethanol is about 17 M). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

Note

The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

Summary

- 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:

$$K = \frac{k_f}{k_r} \tag{15.3.26}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.3.27}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

Label '15.3.1' multiply defined

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n} \tag{15.3.28}$$

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. 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.

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15.4: The Magnitude of an Equilibrium Constant

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 15.4.1*: 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

$$3\,\mathrm{H_2\,(g)} + \mathrm{N_2\,(g)} \longrightarrow 2\,\mathrm{NH_3\,(g)} \tag{15.4.1}$$

can be expressed as

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} \tag{15.4.2}$$

or

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \tag{15.4.3}$$

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

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15.5: The Reaction Quotient, Q - Predicting The Direction of Net Change

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:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.5.1}$$

To understand how information is obtained using a reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$\mathrm{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)}$$

for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[\mathrm{NO_2}^2]}{[\mathrm{N_2O_4}]} \tag{15.5.2}$$

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 15.5.1*: 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 $15.5.1$.

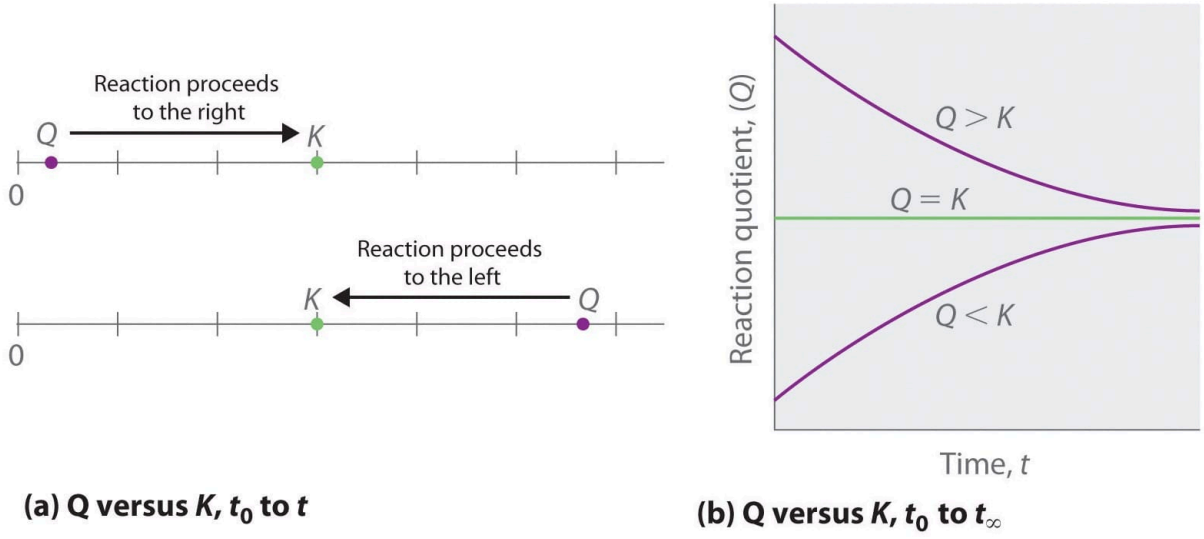


Figure $15.5.1$: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition 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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Example $15.5.1$

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 15.5.1 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 15.5.2

In the water–gas shift reaction introduced in Example 15.5.1, 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:

$$\mathrm{PbCO_3\,(s) \rightleftharpoons PbO\,(s) + CO_2\,(g)} \tag{15.5.3}$$

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 $15.5.3$, 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 $15.5.2$ 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 $15.5.3$ will proceed to the left as written, until $[\mathrm{CO_2}] = K$. Conversely, the point labeled **B** in Figure $15.5.2$ 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 $15.5.3$ will therefore proceed to the right as written, until $[\mathrm{CO_2}] = K$.

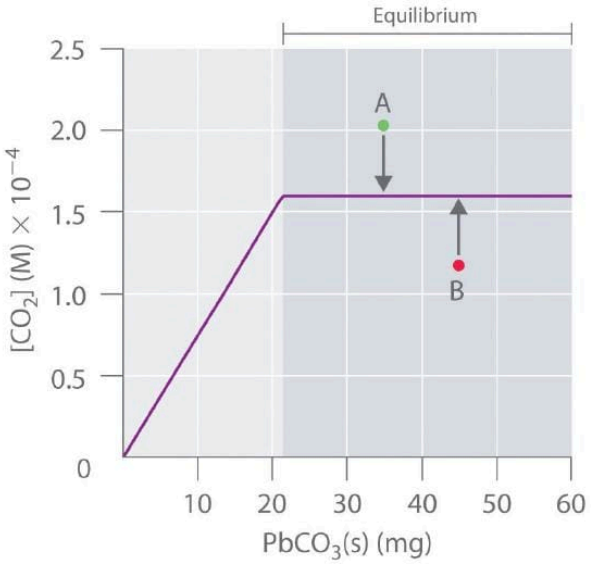


Figure $15.5.2$: The Concentration of Gaseous $\mathrm{CO_2}$ in a Closed System at Equilibrium as a Function of the Amount of Solid $\mathrm{PbCO_3}$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $\mathrm{PbCO_3}$ added, as $\mathrm{PbCO_3}$ decomposes to $\mathrm{CO_2\,(g)}$ 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:

$$\mathrm{CdO\,(s) + H_2\,(g) \rightleftharpoons Cd\,(s) + H_2O\,(g)} \tag{15.5.4}$$

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 15.5.3). 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 15.5.4 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point **A** in Figure 15.5.3 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 15.5.4 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 15.5.3 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 15.5.4 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.

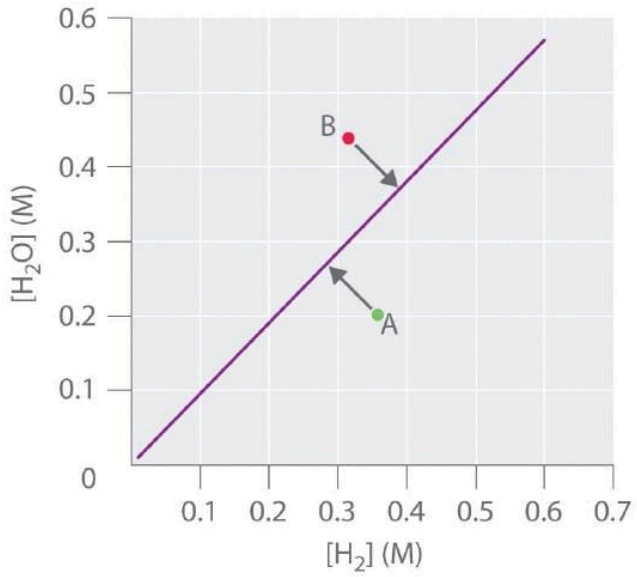


Figure 15.5.3: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of $H_{2(g)}$. Because the 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:

$$\mathrm{NH_4I\,(s) \rightleftharpoons NH_3\,(g) + HI\,(g)} \tag{15.5.5}$$

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 15.5.4. 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 $15.5.4$) corresponds to $Q < K$, and the reaction in Equation $15.5.5$ 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 $15.5.5$) corresponds to $Q > K$, and the reaction in Equation $15.5.5$ 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.

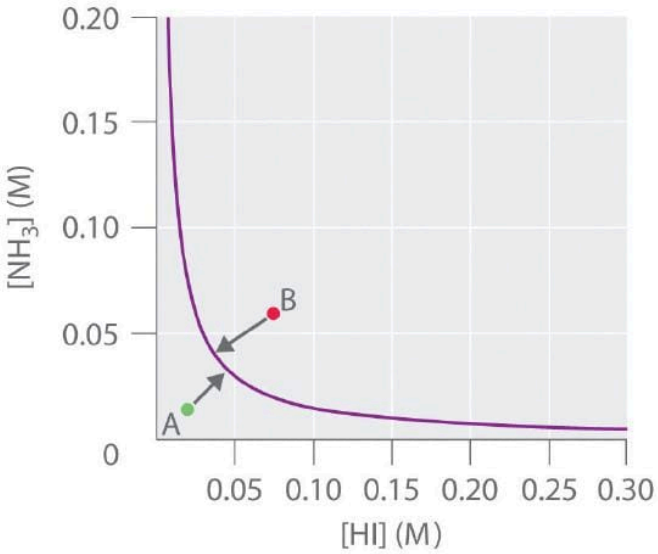


Figure $15.5.4$: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for system in Reaction $15.5.5$ at Equilibrium. Only one equilibrium concentration of $\mathrm{NH_3\,(g)}$ is possible for any given equilibrium concentration of $\mathrm{HI\,(g)}$. In this case, the two are inversely 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 $15.5.2$

$Q = 0.96$. Since (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

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15.6: Altering Equilibrium Conditions - Le Châtelier'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 $15.6.1$ 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 15.6.1: (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:

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \tag{15.6.1}$$

$$K_c = 50.0 \text{ at } 400°C \tag{15.6.2}$$

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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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:

$$2\,\mathrm{NO\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{NO_2\,(g)} \tag{15.6.3}$$

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:

$$\mathrm{N_2\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{NO\,(g)} \tag{15.6.4}$$

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):

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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.

$$\mathrm{H_2\,(g) + I_2\,(g) \;\rightleftharpoons\; 2\,HI\,(g)} \quad \Delta H = -9.4\ \mathrm{kJ\ (exothermic)} \tag{15.6.5}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$\mathrm{H_2\,(g) + I_2\,(g) \;\rightleftharpoons\; 2\,HI\,(g) + heat} \tag{15.6.6}$$

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

$$\mathrm{N_2O_4\,(g) \;\rightleftharpoons\; 2\,NO_2\,(g)} \quad \Delta H = 57.20\ \mathrm{kJ} \tag{15.6.7}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\mathrm{heat + N_2O_4\,(g) \;\rightleftharpoons\; 2\,NO_2\,(g)} \tag{15.6.8}$$

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 15.6.1.

Table 15.6.1: 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 15.6.1

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 15.6.1

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. $\mathbf{SO_2(g)} + \mathrm{Cl_2\,(g)} \rightleftharpoons \mathrm{SO_2Cl_2\,(l)}$: the concentration of $\mathrm{Cl_2}$ is doubled.

Answer a available at the end of this section.

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

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

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)} \rightleftharpoons \mathrm{2\,NH_3\,(g)} \tag{15.6.9}$$

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 15.6.9). 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 15.6.1: 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 15.6.1

$K = \frac{[H_2]}{[HBr]}$; $[H_2]$ 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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15.7: Equilibrium Calculations - Some Illustrative Examples

Learning Objectives

- To solve quantitative problems involving chemical equilibriums.

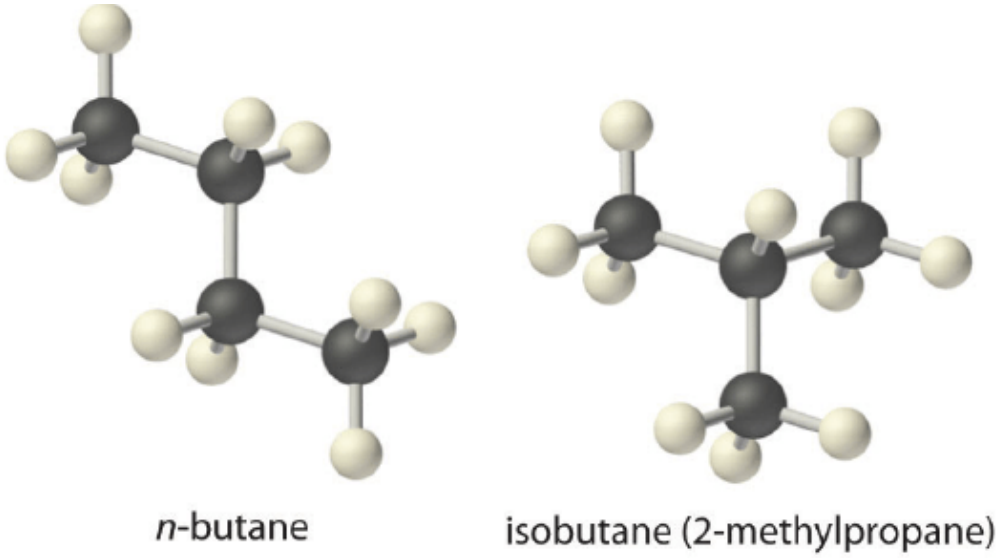
There are two fundamental kinds of equilibrium problems:

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 previously the equilibrium constant for the decomposition of $\mathrm{CaCO_3\,(s)}$ to $\mathrm{CaO\,(s)}$ and $\mathrm{CO_2\,(g)}$ is $K = [\mathrm{CO_2}]$. At 800°C, the concentration of $\mathrm{CO_2}$ in equilibrium with solid $\mathrm{CaCO_3}$ 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:

$$n\text{-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{15.7.1}$$

and the equilibrium constant

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]}. \tag{15.7.2}$$

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,

$$K = \frac{[isobutane]}{[n-butane]} \tag{15.7.3}$$

$$= \frac{0.041\ M}{0.016\ M} \tag{15.7.4}$$

$$= 2.6 \tag{15.7.5}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 15.7.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2\,\mathrm{SO_2\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{SO_3\,(g)}$$

A mixture of $\mathrm{SO_2}$ and $\mathrm{O_2}$ was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ \mathrm{SO_3}$,
- $3.5 \times 10^{-3}\ M\ \mathrm{O_2}$, and
- $3.0 \times 10^{-3}\ M\ \mathrm{SO_2}$.

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 between K and K_p, where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n}$$

$$= 7.9 \times 10^4[(0.08206\ L \cdot atm/mol \cdot K)(800K)]^{-1}$$

$$= 1.2 \times 10^3$$

Exercise 15.7.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$\mathrm{H_2\,(g)} + \mathrm{I_2\,(g)} \rightleftharpoons 2\,\mathrm{HI\,(g)}$$

A mixture of $\mathrm{H_2}$ and $\mathrm{I_2}$ 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:

- $K = 48.8$
- $K_p = 48.8$

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 $15.7.2$ shows one way to do this.

Example 15.7.2

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:

$$2\,\mathrm{NOCl\,(g)} \rightleftharpoons 2\,\mathrm{NO\,(g)} + \mathrm{Cl_2\,(g)}$$

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 $\mathrm{Cl_2}$ 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.

$$2\,\mathrm{NOCl\,(g)} \rightleftharpoons 2\,\mathrm{NO\,(g)} + \mathrm{Cl_2\,(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
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:

$$2\,\mathrm{NOCl\,(g)} \rightleftharpoons 2\,\mathrm{NO\,(g)} + \mathrm{Cl_2\,(g)}$$

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:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M \tag{15.7.6}$$

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:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M \tag{15.7.7}$$

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:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M \tag{15.7.8}$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444M \tag{15.7.9}$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)} \tag{15.7.10}$$

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:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4} \tag{15.7.11}$$

Exercise 15.7.2

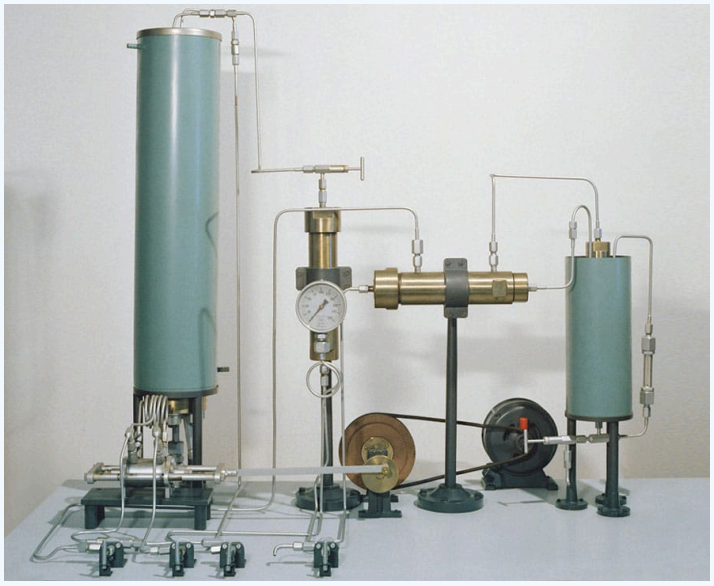
The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ M\ H_2$ and $0.0416\ M\ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \tag{15.7.12}$$

at this temperature? What is K_p?

Answer:

- $K = 0.105$
- $K_p = 2.61 \times 10^{-5}$



The original laboratory apparatus designed by Fritz Haber and Robert Le Rossignol in 1908 for synthesizing ammonia from its elements. A metal catalyst bed, where ammonia was produced, is in the large cylinder at the left. The Haber-Bosch process used for the industrial production of ammonia uses essentially the same process and components but on a much larger scale. Unfortunately, Haber's process enabled Germany to prolong World War I when German supplies of nitrogen compounds, which were used for explosives, had been exhausted in 1914.

YouTube Video

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View this YouTube Video online

Using Q to Find Equilibrium Concentrations: https://youtu.be/-sbeII65Z7w

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 15.7.1), 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 15.7.2.

$$\text{n-butane}(g) \rightleftharpoons \text{isobutane}(g) \tag{15.7.13}$$

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.

$$\text{n-butane}(g) \rightleftharpoons \text{isobutane}(g) \tag{15.7.14}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
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,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6 \tag{15.7.15}$$

Rearranging and solving for x,

$$\begin{aligned} x &= 2.6(1.00 - x) \\ x &= 2.6 - 2.6x \\ x + 2.6x &= 2.6 \\ x &= 0.72 \end{aligned}$$

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:

$$\begin{aligned}[\text{n-butane}]_f &= (1.00 - x)M \\ &= (1.00 - 0.72)M \\ &= 0.28\ M \\ [\text{isobutane}]_f &= (0.00 + x)M \\ &= (0.00 + 0.72)M \\ &= 0.72\ M\end{aligned}$$

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:

$$\begin{aligned}K &= \frac{[\text{isobutane}]}{[\text{n-butane}]} \\ &= \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) \\ &= 2.6\end{aligned}$$

This is the same K we were given, so we can be confident of our results.

Example $15.7.3$ illustrates a common type of equilibrium problem that you are likely to encounter.

Example 15.7.3: water–gas shift

The water–gas shift reaction is important in several chemical processes, such as the production of $\mathrm{H_2}$ for fuel cells. This reaction can be written as follows:

$$\mathrm{H_2\,(g) + CO_2\,(g) \rightleftharpoons H_2O\,(g) + CO\,(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M $\mathrm{H_2}$ and 0.0150 M $\mathrm{CO_2}$ 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 $[\mathrm{H_2}]_i = [\mathrm{CO_2}_i] = 0.0150\ \ M$. 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 $\mathrm{H_2O}$ as x, then $\Delta[\mathrm{H_2O}] = +x$. 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 $\mathrm{H_2O}$, so the change in the CO concentration can be expressed as $\Delta[\mathrm{CO}] = +x$. Similarly, for every 1 mol of $\mathrm{H_2O}$ produced, 1 mol each of $\mathrm{H_2}$ and $\mathrm{CO_2}$ are consumed, so the change in the concentration of the reactants is $\Delta[\mathrm{H_2}] = \Delta[\mathrm{CO_2}] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \tag{15.7.16}$$

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:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150-x)(0.0150-x)} = \frac{x^2}{(0.0150-x)^2} = 0.106 \tag{15.7.17}$$

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,

$$\frac{x^2}{(0.0150-x)^2} = \left(\frac{x}{0.0150-x}\right)^2 = 0.106 \tag{15.7.18}$$

Taking the square root of the middle and right terms,

$$\begin{aligned} \frac{x}{(0.0150-x)} &= (0.106)^{1/2} \\ &= 0.326 \\ x &= (0.326)(0.0150) - 0.326x \\ 1.326x &= 0.00489 \\ x &= 0.00369 = 3.69 \times 10^{-3} \end{aligned}$$

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:

$$\begin{aligned} K &= \frac{[H_2O][CO]}{[H_2][CO_2]} \\ &= \frac{(0.00369)^2}{(0.0113)^2} \\ &= 0.107 \end{aligned}$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

Exercise 15.7.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)} \tag{15.7.19}$$

$K = 54$ 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:

- $[HI]_f = 0.270\ \ M$
- $[H_2]_f = [I_2]_f = 0.037\ \ M$

In Example 15.7.3, 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 15.7.4.

Example 15.7.4

In the water–gas shift reaction shown in Example 15.7.3, a sample containing 0.632 M CO_2 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 $[CO_{2i}] = 0.632\ \ M$ 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 H_2O, so Δ[\ce{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.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \tag{15.7.20}$$

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:

$$\begin{aligned} K &= \frac{[H_2O][CO]}{[H_2][CO_2]} \\ &= \frac{x^2}{(0.570 - x)(0.632 - x)} \\ &= 0.106 \end{aligned}$$

In contrast to Example 15.7.3, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.20x + x^2)$$

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:

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)} \end{aligned}$$

so

$$x = 0.148 \text{ and } -0.290$$

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:

$$\begin{aligned} K &= \frac{[H_2O][CO]}{[H_2][CO_2]} \\ &= \frac{(0.148)^2}{(0.422)(0.484)} \\ &= 0.107 \end{aligned}$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

Exercise 15.7.4

The exercise in Example 15.7.1 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:

- $[H_I]_f = 0.0882\ M$
- $[H_2]_f = 0.156\ M$
- $[I_2]_f = 9.2 \times 10^{-4} M$

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 15.7.5.

Example 15.7.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \tag{15.7.21}$$

with $K_p = 2.0 \times 10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with $\mathrm{N_2}$ and $\mathrm{O_2}$ in the atmosphere (at 1 atm, $P_{\mathrm{N_2}} = 0.78\ atm$ and $P_{\mathrm{O_2}} = 0.21\ atm$?

Given: balanced equilibrium equation and values of K_p, $P_{\mathrm{O_2}}$, and $P_{\mathrm{N_2}}$

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 K_p and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of $\mathrm{O_2}$ is 0.21 atm and that of $\mathrm{N_2}$ 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 $\mathrm{O_2}$ and of $\mathrm{N_2}$ is –x because 1 mol each of $\mathrm{N_2}$ and of $\mathrm{O_2}$ 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.

$$\mathrm{N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)} \tag{15.7.22}$$

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 15.7.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3\,O_2\,(g) \rightleftharpoons 2\,O_3\,(g)$$

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.

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

Finding Equilibrium Concentrations for Reactions with a Small K Value:

https://youtu.be/EyCZTyJvrj8

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 ≥ 103). 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 15.7.6.

Example 15.7.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)} \tag{15.7.23}$$

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 15.7.5. 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,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18} \tag{15.7.24}$$

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:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18} \tag{15.7.25}$$

$$x = 3.6 \times 10^{-19} \tag{15.7.26}$$

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:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18} \tag{15.7.27}$$

This K value agrees with our initial value at the beginning of the example

Exercise 15.7.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$\mathrm{H_2\,(g) + Cl\ 2\,(g) \rightleftharpoons 2\,HCl\,(g)}$$

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:

- $[H_2]_f = 4.8 \times 10^{-32}\ \ M$
- $[Cl_2]_f = 0.135\ \ M$
- $[HCl]_f = 0.514\ \ M$

Summary

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.

Key Takeaway

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.

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?

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 $2A \rightleftharpoons B + C$?
2. The following table shows the reported values of the equilibrium P_{O_2} at three temperatures for the reaction $Ag2O_{(s)} \rightleftharpoons 2Ag_{(s)} + 12O_{2(g)}$, 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 $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$, 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: \[H_{2(g)}+I_{2(g)} \rightleftharpoons 2HI_{(g)}\]. 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:

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)} \tag{15.7.28}$$

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 $A(s) \rightleftharpoons 2B_{(g)} + C_{(g)}$, what is K_p?
7. The decomposition of ammonium carbamate to NH_3 and CO_2 at 40°C is written as $NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$. 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 $SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl2_{(g)}$ 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 $aA \rightleftharpoons bB$, show that $K_p = K(RT)^{\Delta n}$ assuming ideal gas behavior.
10. For the gas-phase reaction I_2 \rightleftharpoons 2I, show that the total pressure is related to the equilibrium pressure by the following equation:

$$P_T = \sqrt{K_p P_{I_2}} + P_{I_2} \tag{15.7.29}$$

11. Experimental data on the system

$$Br_{2(l)} \rightleftharpoons Br_{2(aq)} \tag{15.7.30}$$

are given in the following table. Graph $[Br_2]$ 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

Moles n-butane	Moles Isobutane
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:

$$NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)} \tag{15.7.31}$$

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 $COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl2_{(g)}$ 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:

$$IO^-_{4(aq)} + 2H_2O_{(l)} \rightleftharpoons H_4IO^-_{6(aq)} \tag{15.7.32}$$

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:

$$I_{2(g)} + Br_{2(g)} \rightleftharpoons 2IBr_{(g)} \tag{15.7.33}$$

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

$$C_{(s)} + 12N_{2(g)} + \frac{5}{2}H_{2(g)} \rightleftharpoons CH3NH2(g) \tag{15.7.34}$$

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?

Answers

Exercise 15.7.5

$4.8 \times 10^{-31}\ atm$

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16: ACIDS AND BASES

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

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16.1: Arrhenius Theory: 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

- Anonymous

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16.2: Brønsted-Lowry Theory of 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

The Arrhenius definition of an acid as 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.

Brønsted-Lowry Defintions

- A compound that **donates** a proton to another compound is called a Brønsted-Lowry acid.
- A compound that **accepts** a proton is called a Brønsted-Lowry base.

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Definitions of Acids and Bases: https://youtu.be/r8reN0CSIHw

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):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{16.2.2}$$

$$HF \rightleftharpoons H^+ + F^-$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

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):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{16.2.3}$$

$$OH^- + H^+ \rightleftharpoons H_2O$$

$$H_2O + H^+ \rightleftharpoons H_3O^+$$

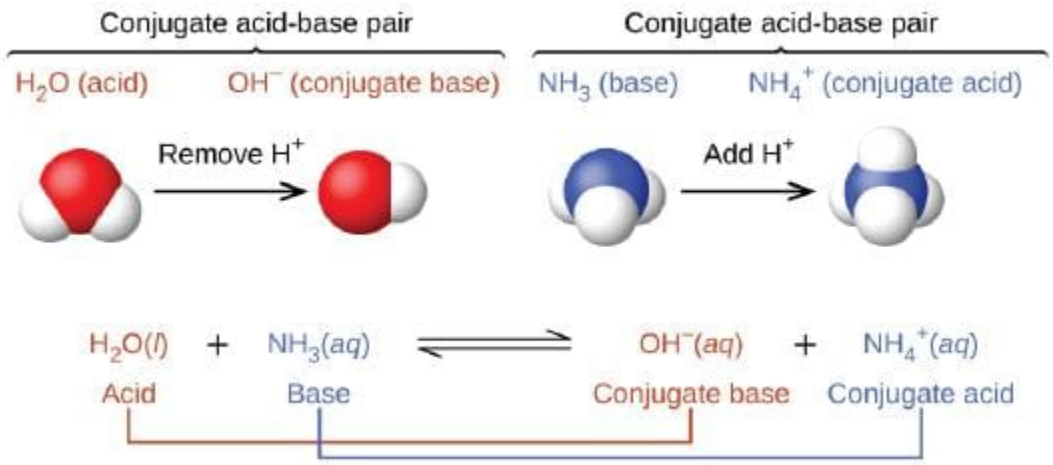
$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

$$S^{2-} + H^+ \rightleftharpoons HS^-$$

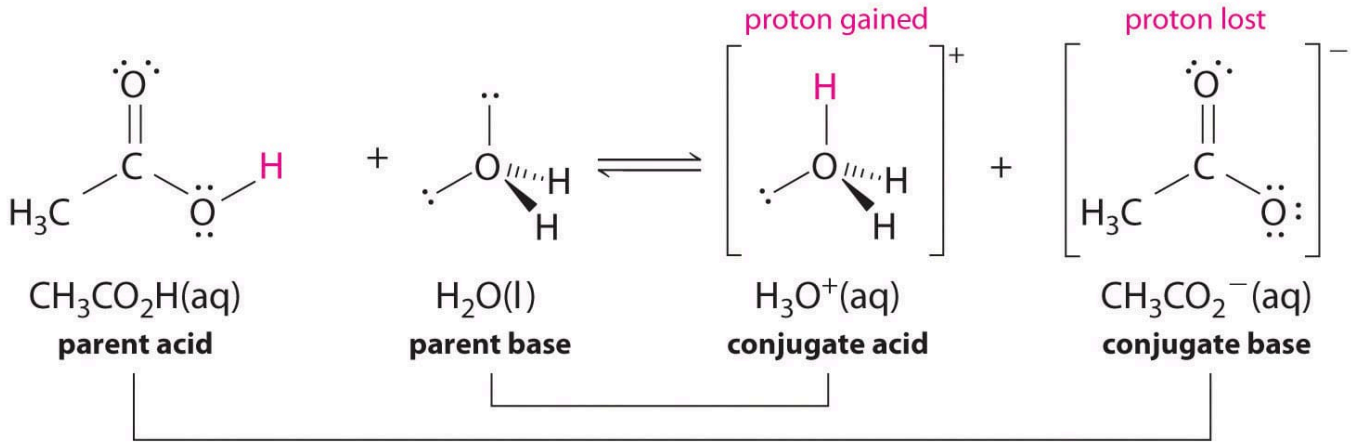
$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

$$F^- + H^+ \rightleftharpoons HF$$

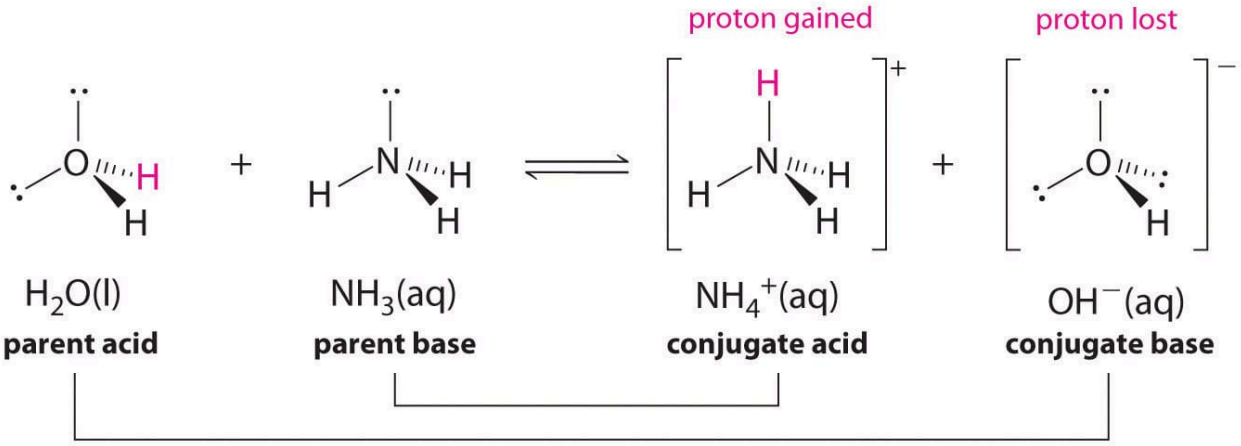
In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is 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^+:



Similarly, in the reaction of acetic acid with water, acetic acid donates a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base. Once again, we have two conjugate acid–base pairs: the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and the parent base and its conjugate acid (H_3O^+/H_2O).



In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-.



YouTube Video

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Conjugate Acid-Base Pairs: https://youtu.be/pPrp3xEQef4

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:

$$\mathrm{HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons CO_3^{2-}\,(aq) + H_3O^+\,(aq)}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

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**:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Example 16.2.1: 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. $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$
b. $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

Exercise 16.2.1

Write separate equations representing the reaction of $H_2PO_4^-$

a. as a base with HBr
b. as an acid with OH^-

Answer a available at the end of this section.

Key Concepts and 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:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

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

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Answers

Exercise 16.2.1

$$\mathrm{H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)}$$

$$\mathrm{H_2PO_4^-}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}_{(l)}$$

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16.3: Self-Ionization of Water and the pH Scale

Learning Objectives

- To understand the autoionization reaction of liquid water.
- To know the relationship among pH, pOH, and pK_w.

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^+):

$$\underset{aicd}{\mathrm{HCl\,(aq)}} + \underset{base}{\mathrm{H_2O\,(l)}} \rightarrow \underset{acid}{\mathrm{H_3O^+\,(aq)}} + \underset{base}{\mathrm{Cl^-\,(aq)}} \tag{16.3.1}$$

In this reaction, HCl is the acid, and water acts as a base by accepting an $\mathrm{H^+}$ ion. The reaction in Equation 16.3.1 is often written in a simpler form by removing $\mathrm{H_2O}$ from each side:

$$\mathrm{HCl\,(aq)} \rightarrow \mathrm{H^+\,(aq)} + \mathrm{Cl^-\,(aq)} \tag{16.3.2}$$

In Equation 16.3.2, the hydronium ion is represented by $\mathrm{H^+\,(aq)}$, although free $\mathrm{H^+}$ ions do not exist in liquid water as this reaction demonstrates:

$$\mathrm{H^+\,(aq)} + \mathrm{H_2O\,(l)} \rightarrow \mathrm{H_3O^+\,(aq)} \tag{16.3.3}$$

Water can also act as an acid, as shown in Equation 16.3.4. In this equilibrium reaction, H_2O donates a proton to NH_3, which acts as a base:

$$\underset{aicd}{\mathrm{H_2O\,(aq)}} + \underset{base}{\mathrm{NH_3\,(aq)}} \rightleftharpoons \underset{acid}{\mathrm{NH_4^+\,(aq)}} + \underset{base}{\mathrm{OH^-\,(aq)}} \tag{16.3.4}$$

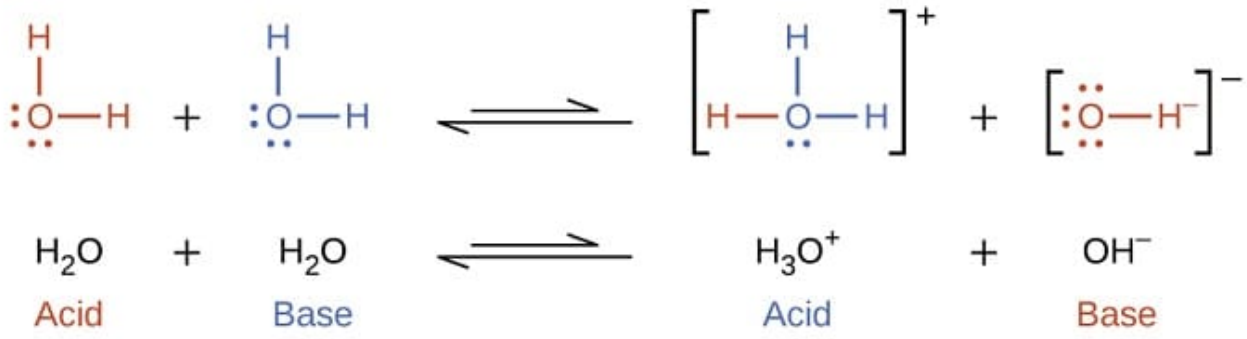
Water is thus termed **amphiprotic**, meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that Equation 16.3.4 is an equilibrium reaction as indicated by the double arrow and hence has an equilibrium constant associated with it.

The Ion-Product Constant of Pure 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:

$$2\,\mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{OH^-\,(aq)} \tag{16.3.5}$$

In pure water, a very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



The equilibrium constant K for this reaction can be written as follows:

$$K_a = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a^2_{H_2O}} \approx \frac{[H_3O^+][HO^-]}{(1)^2} = [H_3O^+][HO^-] \tag{16.3.6}$$

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 liquid 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:

$$K_w = [H_3O^+][HO^-] \tag{16.3.7}$$

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:

$$[H_3O^+] = [OH^-] = 1.003 \times 10^{-7}\ M \tag{16.3.8}$$

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

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14} \tag{16.3.9}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C.Thus, to three significant figures, $K_w = 1.01 \times 10^{-14}\ M$ *at room temperature*. 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.

Example 16.3.1: 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, $[\mathrm{H_3O^+}] = [\mathrm{OH^-}]$. At 25 °C:

$$\begin{aligned} K_{\text{w}} &= [\text{H}_3\text{O}^+][\text{OH}^-] \\ &= [\text{H}_3\text{O}^+]^2 \\ &= [\text{OH}^-]^2 \\ &= 1.0 \times 10^{-14} \end{aligned}$$

So:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

Exercise 16.3.1

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 available at the end of this section.

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. Example 16.3.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

Example 16.3.2: The Inverse Proportionality of Hydronium and Hydroxide Concentrations

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:

$$2\,\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+{}_{(aq)} + \text{OH}^-{}_{(aq)}$$

and

$$K_{\text{w}} = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the k_w expression yields that $[\text{OH}^-]$ is directly proportional to the inverse of $[\text{H}_3\text{O}^+]$:

$$[\text{OH}^-] = \frac{K_{\text{w}}}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

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 $[\text{OH}^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_{\text{w}} = [\text{H}_3\text{O}^+][\text{OH}^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 16.3.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer available at the end of this section.

YouTube Video

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Self-Ionization of Water (Kw): https://youtu.be/RMpO0rqUnFg

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:

$$pH = -\log_{10}[\mathrm{H}^+] \tag{16.3.10}$$

$$[\mathrm{H}^+] = 10^{-pH} \tag{16.3.11}$$

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 $[\mathrm{H_3O^+}] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[\mathrm{H_3O^+}] < 1.0 \times 10^{-7}$).

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 $[\mathrm{OH}^-]$ are related as follows:

$$pOH = -\log_{10}[\mathrm{OH}^-] \tag{16.3.12}$$

$$[\mathrm{OH}^-] = 10^{-pOH} \tag{16.3.13}$$

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 ???:

$$-\log K_w = pK_w \tag{16.3.14}$$

$$= -\log([H_3O^+][OH^-]) \tag{16.3.15}$$

$$= (-\log[H_3O^+]) + (-\log[OH^-]) \tag{16.3.16}$$

$$= pH + pOH \tag{16.3.17}$$

Thus at any temperature, $pH + pOH = pK_w$, so at 25°C, where $K_w = 1.0 \times 10^{-14}$ and $pH + pOH = 14.00$. 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.

For any neutral solution, pH + pOH = 14.00 (at 25°C) with pH=pOH=7.

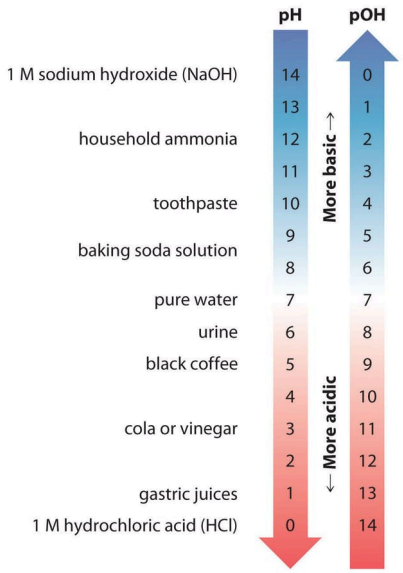


Figure 16.3.1: The Inverse Relationship between the pH and pOH Scales. As pH decreases, $[H^+]$ and the acidity increase. As pOH increases, $[OH^-]$ and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic. (CC BY; OpenStax)

Example 16.3.3

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 pKw by taking the negative logarithm of K_w.
B. For a neutral aqueous solution, $[H_3O^+] = [OH^-]$. Use this relationship and Equation ??? 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 $x = [H_3O^+] = [OH^-]$:

$$\begin{aligned} K_w &= [\mathrm{H_3O^+}][\mathrm{OH^-}] \\ &= (x)(x) \\ &= x^2 \\ x &= \sqrt{K_w} \\ &= \sqrt{4.99 \times 10^{-13}} \\ &= 7.06 \times 10^{-7}\ M \end{aligned}$$

Because x is equal to both $[\mathrm{H_3O^+}]$ and $[\mathrm{OH^-}]$,

$$\begin{aligned} pH = pOH &= -\log(7.06 \times 10^{-7}) \\ &= 6.15\ (\text{to two decimal places}) \end{aligned}$$

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:

$$pK_w = pH + pOH = y + y = 2y$$

$$y = \frac{pK_w}{2} = \frac{12.302}{2} = 6.15 = pH = pOH$$

Exercise 16.3.3

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.

YouTube Video

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Introduction to pH: https://youtu.be/pQOa3bb5YEE

Summary

- For any neutral solution, $pH + pOH = 14.00$ (at 25°C) and $pH = \frac{1}{2}pK_w$.
- 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:

$$pK_w = pH + pOH$$

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 (K_w) and is defined as $K_w = [H_3O^+][OH^-]$. At 25°C, K_w is 1.01×10^{-14}; hence $pH + pOH = pK_w = 14.00$. 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.

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

autoionization
: reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

ion-product constant for water (K_w)
: equilibrium constant for the autoionization of water

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Answers

Exercise 16.3.1

$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = 4.9 \times 10^{-7}\ M$

Exercise 16.3.2

$$[\mathrm{H_3O^+}] = 1 \times 10^{-11} M$$

Exercise 16.3.3

$pK_w = 13.45$ and $pH = pOH = 6.73$

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16.4: Strong Acids and Strong Bases

Learning Objectives

- Give the names and formulas of some strong acids and bases.
- Explain the pH scale, and convert pH and concentration of hydronium ions.
- Evaluate solution pH and pOH of strong acids or bases.

Acids and bases that are completely ionized when dissolved in water are called **strong acids** and **strong bases** There are only a few strong acids and bases, and everyone should know their names and properties. These acids are often used in industry and everyday life. The concentrations of acids and bases are often expressed in terms of pH, and as an educated person, you should have the skill to convert concentrations into pH and pOH. The pH is an indication of the hydrogen ion concentration, $[H^+]$.

Strong Acids

Strong acids are acids that are completely or nearly 100% ionized in their solutions; Table $16.4.1$ includes some common strong acids. Hence, the ionization in Equation $16.4.1$ for a strong acid HA can be represented with a single arrow:

$$HA\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + A^-\,(aq) \tag{16.4.1}$$

Water is the base that reacts with the acid HA, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. By definition, a strong acid yields 100% of H_3O^+ and A^- when the acid ionizes in water. Table $16.4.1$ lists several strong acids.

Table $16.4.1$: Some of the common strong acids and bases are listed here.

Strong Acids	Strong Bases
perchloric acid ($HClO_4$)	lithium hydroxide ($LiOH$)
hydrochloric acid (HCl)	sodium hydroxide ($NaOH$)
hydrobromic acid (HBr)	potassium hydroxide (KOH)
hydroiodic acid (HI)	calcium hydroxide ($Ca(OH)_2$)
nitric acid (HNO_3)	strontium hydroxide ($Sr(OH)_2$)
sulfuric acid (H_2SO_4)	barium hydroxide ($Ba(OH)_2$)

For a strong acid, $[H^+]$ = $[A^-]$ = concentration of acid if the concentration is much higher than $1 \times 10^{-7}\ M$. However, for a very dilute strong acid solution with concentration less than $1 \times 10^{-7}\ M$, the pH is dominated by the **autoionization of water**

$$H_2O \rightleftharpoons H^+ + OH^- \tag{16.4.2}$$

Example $16.4.1$

Calculate the pH of a solution with $1.2345 \times 10^{-4}\ M HCl$, a strong acid.

Solution

The solution of a strong acid is completely ionized. That is, this equation goes to completion

$$HCl\,(aq) \longrightarrow H\,(aq) + Cl^-\,(aq)$$

Thus, $[H^+] = 1.2345 \times 10^{-4}$.

$$\text{pH} = -\log(1.2345 \times 10^{-4}) = 3.90851$$

Exercise 16.4.1

What is the pH for a solution containing 1.234 M $[\text{HCl}]$?

Answer available at the end of this section.

Example 16.4.2

Calculate the pH of a stock HCl solution that is 32% by mass HCl.

Solution

The density of such a solution is needed before we can calculate the pH. Since the density is not on the label, we need to find it from the Material Safety Data Sheet, which gives the specific gravity of 1.150. Thus, the amount of acid in 1.0 L is 1150 g.

$$\begin{aligned}\text{The amount of HCl} &= 1000 \times 1.150 \times 0.32 \\ &= 368 \text{ g} \left(\frac{1 \text{ mol}}{36.5 \text{ g}} \leftarrow \text{molar mass of HCl}\right) \\ &= 10.08 \text{ M} \\ &= [\text{H}^+]\end{aligned}$$

$$\text{pH} = -\log(10.08) = -1.003$$

Discussion

Yes, pH have negative values if $[\text{H}^+] > 1.0$

Exercise 16.4.2

Check out the information on nitric acid, a strong acid, and calculate the pH of a stock nitric acid solution.

Example 16.4.3

Calculate the pH of a solution containing $1.00 \times 10^{-7}\ M$ of the strong acid HCl.

Solution

$[\text{H}^+] = 1.0 \times 10^{-7}\ M$ from the strong acid, and if *x* is the amount from the ionization of water, then we have the equilibrium due to the **autoionization** of water. We can model this with an ICE table.

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

ICE Table	$H_2O_{(l)}$	$H^+_{(aq)}$	$OH^-_{(aq)}$
Initial	-	1×10^{-7}	0
Change	-	+x	+x
Equilibrium	-	$1 \times 10^{-7} + x$	x

Recall that $K_w = [\text{H}^+]\ [\text{OH}^-\ ] = 1 \times 10^{-14}$, due to the ionization equilibrium of water in the solution:

$$(1.00 \times 10^{-7} + x)x = 1 \times 10^{-14}$$

$$x^2 + 1.00 \times 10^{-7}x - 1.00 \times 10^{-14} = 0$$

Solving this equation for x from the quadratic equation results in

$$x = \frac{-1.00 \times 10^{-7} \pm \sqrt{1.00 \times 10^{-14} + (4)(1)(1.00 \times 10^{-14})}}{2}$$
$$= 0.61 \times 10^{-7}$$

only the additive root is physical (positive concentration); therefore

$$[\mathrm{H^+}] = (1.00 + 0.61) \times 10^{-7}\ M$$
$$\mathrm{pH} = -\log(1.61 \times 10^{-7})$$
$$= 6.79$$

Discussion

If you require only 1 significant figure, the pH is about 7.

Strong Bases

Strong bases are completely ionized in solution. Table $16.4.1$ includes some common strong bases. For example, KOH dissolves in water in the reaction

$$\mathrm{KOH} \rightarrow \mathrm{K^+ + OH^-}$$

Relative to the number of strong acids, there are fewer number of strong bases and most are alkali hydroxides. Calcium hydroxide is considered a strong base, because it is completely, almost completely, ionized. However, the solubility of calcium hydroxide is very low. When $\mathrm{Ca(OH)_2}$ dissolves in water, the ionization reaction is as follows:

$$\mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca^{2+} + 2\,OH^-}$$

Because of the stoichiometry of calcium hydroxide, upon dissociation, the concentration of $\mathrm{OH^-}$ will be twice the concentration of $\mathrm{Ca^{2+}}$:

$$[\mathrm{OH^-}] = 2[\mathrm{Ca^{2+}}]$$

Example 16.4.4

Calculate the pOH of a solution containing $1.2345 \times 10^{-4}\ M\ \mathrm{Ca(OH)_2}$.

Solution

Based on complete ionization of

$$\mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca^{+2} + 2\,OH^-}$$

$$[\mathrm{OH^-}] = 2 \times 1.2345 \times 10^{-4}$$
$$= 2.4690 \times 10^{-4}\ M$$
$$\mathrm{pOH} = -\log(2.4690 \times 10^{-4})$$
$$= 3.6074$$

Exercise 16.4.4

The molar solubility of calcium hydroxide is 0.013 M $Ca(OH)_2$. Calculate the pOH.

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

Calculating pH in Strong Acid or Strong Base Solutions: https://youtu.be/NNTptn7hV2s

Questions

1. What is the pH of a solution containing 0.01 M HNO_3?
2. What is the pH of a solution containing 0.0220 M $Ba(OH)_2$? Give 3 significant figures.
3. Exactly 1.00 L solution was made by dissolving 0.80 g of $NaOH$ in water. What is $[H^+]$? (Atomic mass: Na, 23.0; O, 16.0; H, 1.0)
4. What is the pH for a solution which is 0.050 M HCl?
5. Which of the following is usually referred to as strong acid in water solution?

$$HF,\ HNO_2,\ H_2CO_3,\ H_2S,\ HSO_4^-,\ Cl^-,\ HNO_3,\ HCN$$

Solutions

1. ***Answer*** 2
   Hint...
   You do not need a calculator to evaluate $-\log(0.01) = 2$
2. ***Answer*** 12.64
   Hint...
   $Ba(OH)_2 \rightarrow Ba^{2+} + 2\,OH^-$
3. ***Answer*** 5.0×10^{-13}

   Hint...
   $[OH^-] = \frac{0.80}{40} = 0.020\ M$; $[H^+] = \frac{1.0 \times 10^{-14}}{0.020} = 5 \times 10^{-13} M$. The pH is 12.30.
4. ***Answer*** 1.3
   Hint...
   This solution contains 1.83 g of HCl per liter. $[H^+] = 0.050$.
5. ***Answer*** HNO_3
   Consider...
   All others are weak acids

Contributors and Attributions

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Answers

Exercise 16.4.1

pH = -0.0913

Exercise 16.4.4

pOH = 1.58

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16.5: Weak Acids and Weak 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, the concentration of water is essentially constant for all reactions in aqueous solution, so $[H_2O]$ in Equation 16.5.2 can be incorporated into a new quantity, the acid ionization constant (K_a), also called the acid dissociation constant:

$$K_a = K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]} \tag{16.5.3}$$

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 16.5.3. 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 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:

$$\mathrm{B\,(aq) + H_2O\,(l) \rightleftharpoons BH^+\,(aq) + OH^-\,(aq)} \tag{16.5.4}$$

The equilibrium constant for this reaction is the **base ionization constant** (K_b), also called the base dissociation constant:

$$K_b = K[H_2O] = \frac{[BH^+][OH^-]}{[B]} \tag{16.5.5}$$

Once again, the concentration of water is constant, so it does not appear in the equilibrium constant expression; instead, it is included in the K_b. 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 (recall that the equilibrium constant for the sum of two reactions is the product of the equilibrium constants for the individual reactions):

$$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}} \quad K_a = [H^+]\,\cancel{[CN^-]} \,/\, \cancel{[HCN]} \tag{16.5.10}$$

$$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}} \quad K_b = [OH^-]\,\cancel{[HCN]} \,/\, \cancel{[CN^-]} \tag{16.5.11}$$

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \quad K = K_a \times K_b = [H^+][OH^-] \tag{16.5.12}$$

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:

$$K_aK_b = K_w \tag{16.5.13}$$

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 pK_w, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{16.5.14}$$

$$K_a = 10^{-pK_a} \tag{16.5.15}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{16.5.16}$$

$$K_b = 10^{-pK_b} \tag{16.5.17}$$

Similarly, Equation 16.5.13, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{16.5.18}$$

At 25°C, this becomes

$$pK_a + pK_b = 14.00 \tag{16.5.19}$$

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:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base}$$

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:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow\rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{16.5.20}$$

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 ($\mathrm{CH_3CH_2CH_2CO_2}^-$). 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 16.5.13. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equation 16.5.18 and Equation 16.5.19. Use the relationships $pK = -\log K$ and $K = 10{-}pK$ (Equations 16.5.14 and 16.5.16) 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 16.5.19: $pK_a + pK_b = \mathrm{pKw} = 14.00$. Substituting the pK_a and solving for the pK_b,

$$\begin{aligned} 4.83 + pK_b &= 14.00 \\ pK_b &= 14.00 - 4.83 \\ &= 9.17 \end{aligned}$$

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 16.5.13: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$\begin{aligned} K_a(5.4 \times 10^{-4}) &= 1.01 \times 10^{-14} \\ K_a &= 1.9 \times 10^{-11} \end{aligned}$$

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:

$$\begin{aligned} pK_b &= -\log(5.4 \times 10^{-4}) \\ &= 3.27 \end{aligned}$$

$$\begin{aligned} pKa + pK_b &= 14.00 \\ pK_a &= 10.73 \\ K_a &= 10^{-pK_a} \\ &= 10^{-10.73} \\ &= 1.9 \times 10^{-11} \end{aligned}$$

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.

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 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.

Note: Leveling Effect

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 $\mathrm{NaNH_2}$ (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 $\mathrm{OH^-}$ and the corresponding cation:

$$\mathrm{K_2O\,(s) + H_2O\,(l) \longrightarrow 2\,OH^-\,(aq) + 2\,K^+\,(aq)}$$

$$\mathrm{NaOCH_3\,(s) + H_2O\,(l) \longrightarrow OH^-\,(aq) + Na^+\,(aq) + CH_3OH\,(aq)}$$

$$\mathrm{NaNH_2\,(s) + H_2O\,(l) \longrightarrow OH^-\,(aq) + Na^+\,(aq) + NH_3\,(aq)}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium ($\mathrm{CH_3Li}$).

YouTube Video

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Calculating the pH of Weak Acids and Weak Bases: https://youtu.be/zr1V1THJ5P0

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. 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.

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.

Key Equations

- Acid ionization constant:

$$K_a = K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base ionization constant:

$$K_b = K[H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w$$

- 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:

$$pK_a + pK_b = pK_w$$
$$pK_a + pK_b = 14.00 \text{ at } 25^\circ\text{C}$$

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

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16.6: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

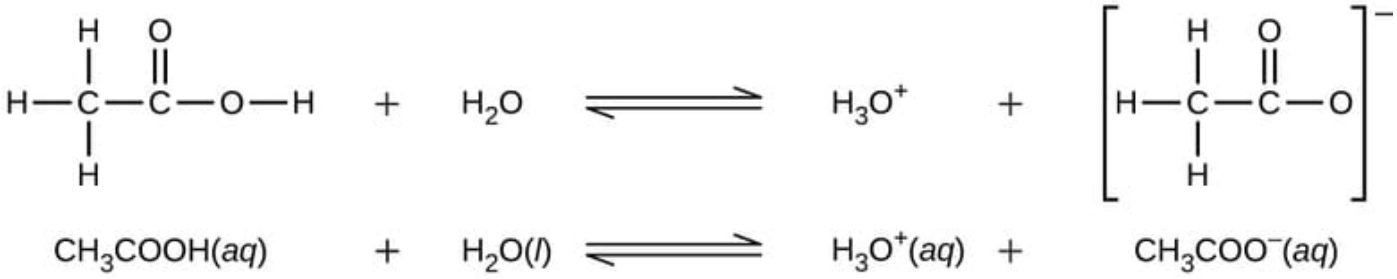
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, $\mathrm{HNO_3}$, and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$

$$\mathrm{HNO_3}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3^-}(aq)$$

$$\mathrm{HCN}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{CN^-}(aq)$$

Even though it contains four hydrogen atoms, acetic acid, $\mathrm{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($-\mathrm{COOH}$) reacts with bases:



This image contains two equilibrium reactions. The first shows a C atom bonded to three H atoms and another C atom. The second C atom is double bonded to an O atom and also forms a single bond to another O atom. The second O atom is bonded to an H atom. There is a plus sign and then the molecular formula H subscript 2 O. An equilibrium arrow follows the H subscript 2 O. To the right of the arrow is H subscript 3 O superscript positive sign. There is a plus sign. The final structure shows a C atom bonded the three H atoms and another C atom. This second C atom is double bonded to an O atom and single bonded to another O atom. The entire structure is in brackets and a superscript negative sign appears outside the brackets. The second reaction shows C H subscript 3 C O O H (a q) plus H subscript 2 O (l) equilibrium arrow H subscript 3 O (a q) plus C H subscript 3 C O O superscript negative sign (a q).

Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- **The first ionization is**

$$\mathrm{H_2SO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq)$$

with $K_{\mathrm{a1}} > 10^2$; *complete dissociation.*

- **The second ionization is**

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq)$$

with $K_{\mathrm{a2}} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution

that contains a mixture of acids. Carbonic acid, H_2CO_3, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

with

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

with

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = 4.7 \times 10^{-11}$$

$K_{H_2CO_3}$ is larger than $K_{HCO_3^-}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the HCO_3^- formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 16.6.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[H_3O^+]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\ M$?

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

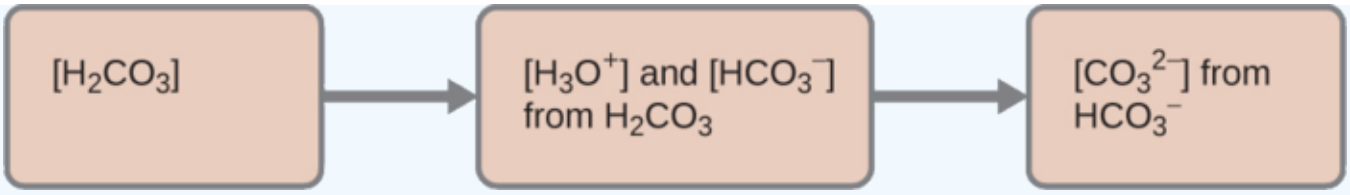
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \quad K_{a2} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than HCO_3^-, so H_2CO_3 is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. Using the customary four steps, we determine the concentration of H_3O^+ and HCO_3^- produced by ionization of H_2CO_3.
2. Then we determine the concentration of CO_3^{2-} in a solution with the concentration of H_3O^+ and HCO_3^- determined in (1).

To summarize:



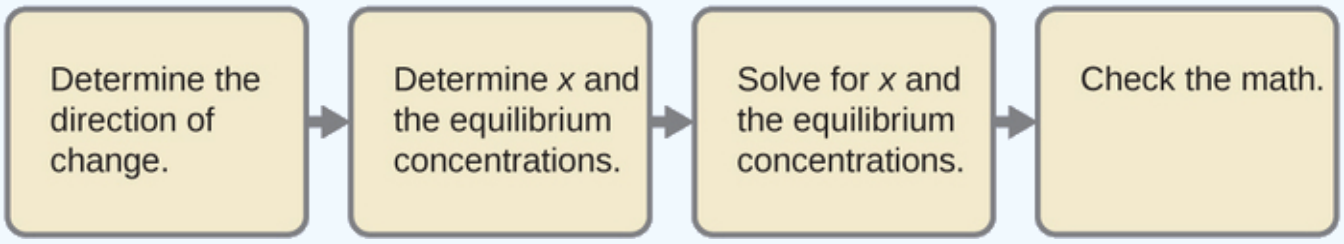
Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “left bracket H subscript 2 C O subscript 3 right bracket.” The second is labeled “left bracket H subscript 3 O superscript plus right bracket and left bracket H C O subscript 3 superscript negative right bracket from H subscript 2 C O subscript 3.” The third is labeled “left bracket C O subscript 3 superscript 2 negative right bracket from H C O subscript 3 superscript negative.”

1. First Ionization: Determine the concentrations of $\mathrm{H_3O^+}$ *and* $\mathrm{HCO_3^-}$.

Since equilibrium step 1 is has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for equilibrium step 2, we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{\mathrm{a1}} = 4.3 \times 10^{-7}$$

As for the ionization of any other weak acid:



Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “Determine the direction of change.” The second is labeled “Determine x and the equilibrium concentrations.” The third is labeled “Solve for x and the equilibrium concentrations.” The fourth is labeled “Check the math.”

An abbreviated table of changes and concentrations shows:

Abbreviated table of changes and concentrations

ICE Table	$\mathrm{H_2CO_3}(aq)$	$\mathrm{H_2O}(l)$	$\mathrm{H_3O^+}(aq)$	$\mathrm{HCO_3^-}(aq)$
Initial (M)	$0.033\ M$	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{\mathrm{H_2CO_3}} = \frac{[H3O+][HCO3-]}{[H2CO3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[\mathrm{H_2CO_3}] = 0.033\ M$$

$$[\mathrm{H_3O^+}] = [\mathrm{HCO_3^-}\ ] = 1.2 \times 10^{-4}\ M$$

2. Second Ionization: Determine the concentration of CO_3^{2-} *in a solution at equilibrium.*

Since the equilibrium step 1 is has a much bigger K_a than equilibrium step 2, we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the equilibrium step 2:

$$\mathrm{HCO_3}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{CO_3}^{2-}(aq)$$

ICER Table for the equilibrium step 2*:*

ICE Table	$\mathrm{HCO_3}^-(aq)$	$\mathrm{H_2O}(l)$	$\mathrm{H_3O}^+(aq)$	$\mathrm{CO_3}^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4}\ M$	-	$1.2 \times 10^{-4}\ M$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4}\ M - y$	-	$1.2 \times 10^{-4}\ M + y$	y

$$K_{\mathrm{HCO_3}^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]}$$
$$= \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{\mathrm{HCO_3}^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[\mathrm{CO_3}^{2-}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the $\mathrm{H_2CO_3}$ in a 0.033-*M* solution ionizes slightly and at equilibrium $[\mathrm{H_2CO_3}] = 0.033\ M$, $[\mathrm{H_3O}^+] = 1.2 \times 10^{-4}$, and $[\mathrm{HCO_3}^-] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[\mathrm{CO_3}^{2-}] = 5.6 \times 10^{-11}\ M$.

Exercise 16.6.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 *M*. Calculate $[\mathrm{H_3O}^+]$, $[\mathrm{HS}^-]$, and $[\mathrm{S}^{2-}]$ in the solution:

$$\mathrm{H_2S}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{HS}^-(aq) \quad K_{\mathrm{a1}} = 8.9 \times 10^{-8}$$

$$\mathrm{HS}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \blacksquare(aq) \quad K_{\mathrm{a2}} = 1.0 \times 10^{-19}$$

Answer available at the end of this section.

Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$\mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{H_2PO_4}^-(aq)$$

with $K_{\mathrm{a1}} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$\mathrm{H_2PO_4}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{HPO_4}^{2-}(aq)$$

with $K_{a2} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$\mathrm{HPO_4}^{2-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{PO_4}^{3-}(aq)$$

with $K_{a3} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$\mathrm{H_2O}(l) + \mathrm{CO_3}^{2-}(aq) \rightleftharpoons \mathrm{HCO_3}^-(aq) + \mathrm{OH}^-(aq)$$

and

$$\mathrm{H_2O}(l) + \mathrm{HCO_3}^-(aq) \rightleftharpoons \mathrm{H_2CO_3}(aq) + \mathrm{OH}^-(aq)$$

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Glossary

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

monoprotic acid
: acid containing one ionizable hydrogen atom per molecule

stepwise ionization
: process in which an acid is ionized by losing protons sequentially

triprotic acid
: acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

Answers

Exercise 16.6.2**: Hydrogen Sulfide**

$[\mathrm{H_2S}] = 0.1M$, $[\mathrm{H_3O}^+] = [HS^-] = 0.0001\ M$, $[S^{2-}] = 1 \times 10^{-19}\ M$

We note that the concentration of the sulfide ion is the same as K_{a2}. This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

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16.7: Ions as Acids and Bases

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

We can also use the relative strengths of conjugate acid–base pairs to understand the acid–base properties of solutions of salts. 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 $\mathrm{CH_3CO_2H}$, a weak acid, with NaOH, a strong base:

$$\underset{acid}{\mathrm{CH_3CO_2H\,(l)}} + \underset{base}{\mathrm{NaOH\,(s)}} \xrightarrow{\mathrm{H_2O}} \underset{salt}{\mathrm{H_2OCH_3CO_2Na\,(aq)}} + \underset{water}{\mathrm{H_2O\,(l)}} \tag{16.7.1}$$

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.

$$\mathrm{CN^-\,(aq) + H_2O\,(l) \rightleftharpoons HCN\,(aq) + OH^-\,(aq)} \tag{16.7.2}$$

$$\mathrm{CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)} \tag{16.7.3}$$

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 E1 and E2, 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. 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:

$$\mathrm{NH_4^+\,(aq) + H_2O\,(l) \rightleftharpoons NH_3\,(aq) + H_3O^+\,(aq)} \tag{16.7.4}$$

$$\mathrm{C_5H_5NH^+\,(aq) + H_2O\,(l) \rightleftharpoons C_5H_5NH\,(aq) + H_3O^+\,(aq)} \tag{16.7.5}$$

Figure 16.7.2 shows 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.

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 Figure 16.9, 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.

YouTube Video

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Ions as Acids and Bases: https://youtu.be/XYAGNonPSow

Acidic Metal Ions

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 (Figure $16.7.1a$). 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.

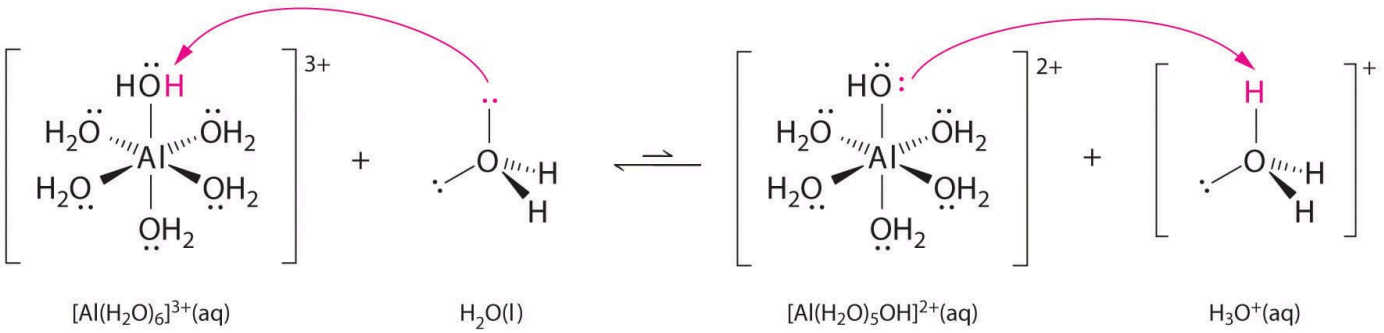


Figure $16.7.1$

Second, the positive charge on the Al^{3+} ion attracts electron density from the oxygen atoms of the water molecules, which decreases the electron density in the $\mathrm{O{-}H}$ bonds, as shown in Figure $16.7.1b$. 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.

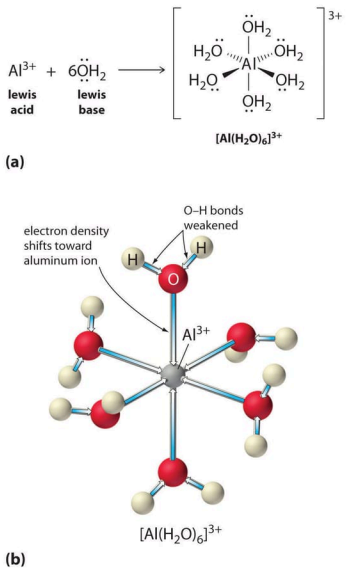


Figure 16.7.2: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron 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.

The magnitude of this effect depends on the following two factors (Figure 16.7.3):

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.

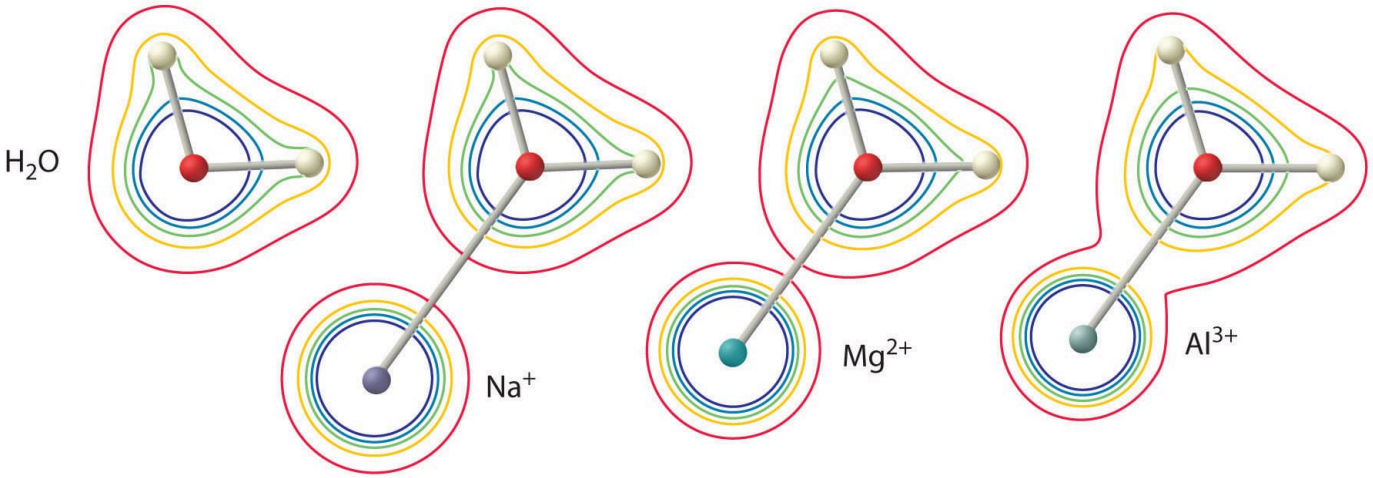


Figure 16.7.3: The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^{+}, Mg^{2+}, and Al^{3+} ions. These contour 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:

$$[Al(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H^{+}_{(aq)} \tag{16.7.6}$$

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.

Acidic Metal Ions

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.

Hydrolysis

A hydrolysis reaction is an acid–base reaction.

Example 16.7.1

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:

$$Cr(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons Cr(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_(aq) \tag{16.7.7}$$

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 16.7.1

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.

Answers

Exercise 16.7.1

neutral

acidic

basic (due to the reaction of HS^- with water to form H_2S and OH^-)

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16.8: Molecular Structure and Acid-Base Behavior

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:

$$H_2O(14.00 = pK_w) < H_2S(7.05) < H_2Se(3.89) < H_2Te(2.6) \tag{16.8.1}$$

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:

$$CH_4(\ 50) \ll NH_3(\ 36) < H_2O(14.00) < HF(3.20) \tag{16.8.2}$$

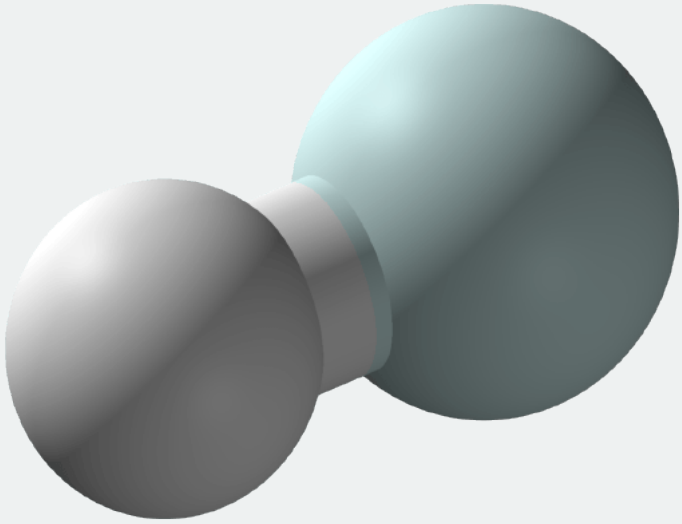
Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH_4 is CH_3^-, and the conjugate base of HF is F^-. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the F^- ion than 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:

$$HOX_{(aq)} \rightleftharpoons H^+_{(aq)} + OX^-(aq) \tag{16.8.3}$$

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 $16.8.1$, 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 $16.8.1$ 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 $16.8.1$ and Figure $16.8.2$, 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.

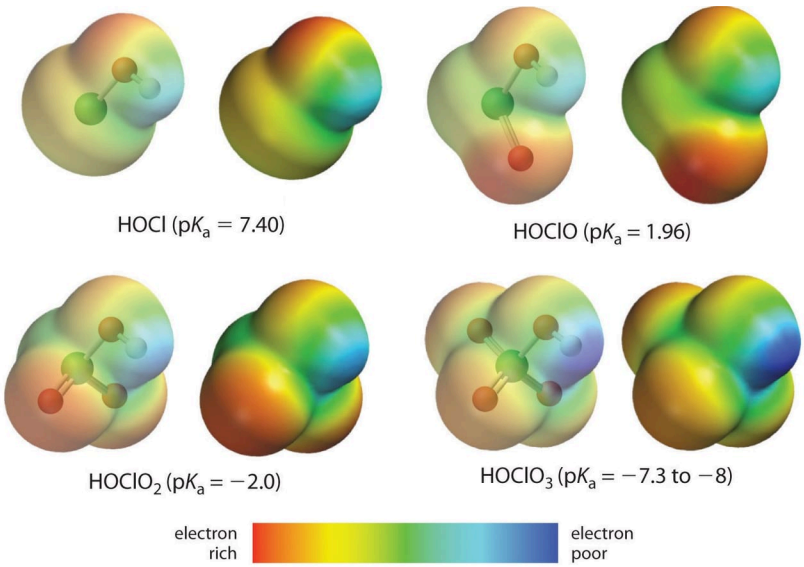
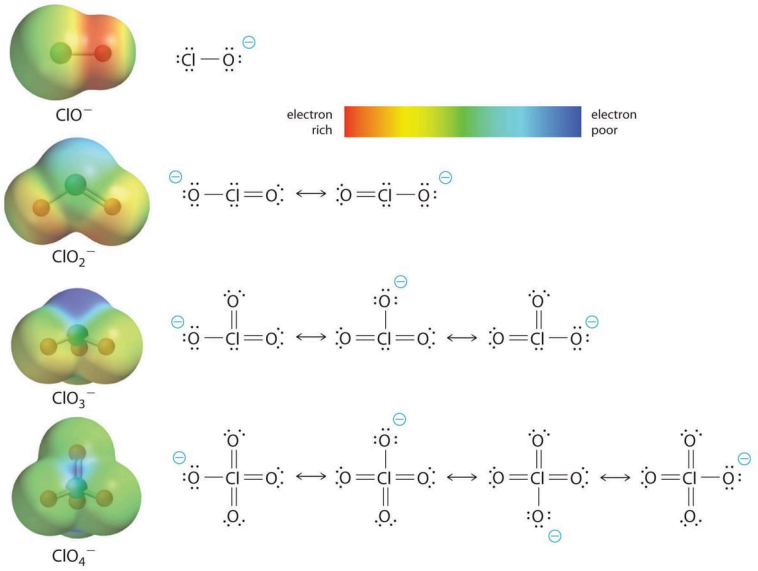


Figure $16.8.1$: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit. These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron 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 $16.8.2$, 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.

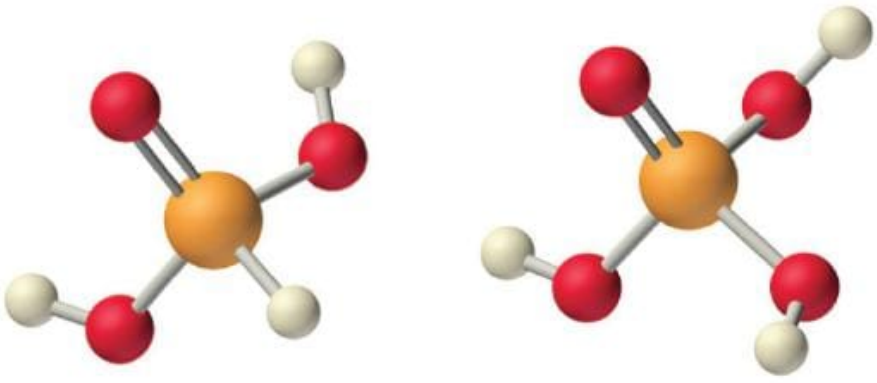
Electron delocalization in the conjugate base increases acid strength.

The electrostatic potential plots in Figure $16.8.2$ 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 $16.8.2$). 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 16.8.1 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 16.8.1: 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

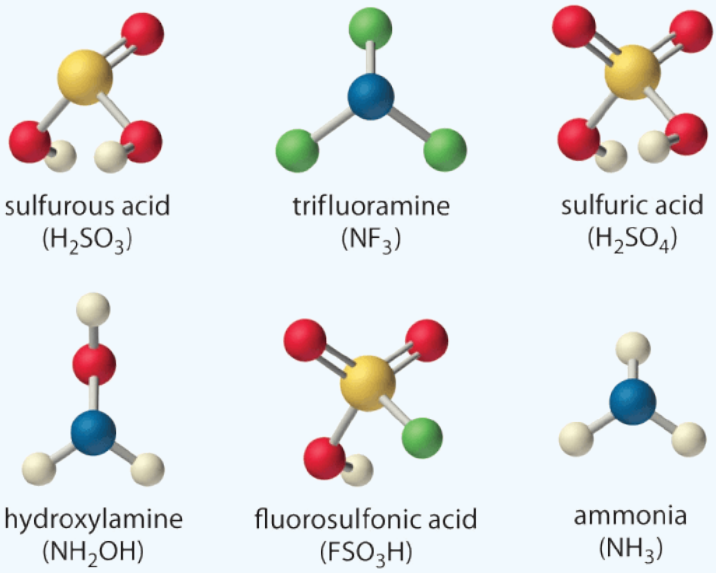
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $-\mathrm{CH_3}$ group of acetic acid by a $-\mathrm{CF_3}$ group results in about a 10,000-fold increase in acidity!

Example 16.8.1

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 16.8.1

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 16.8.1

$HClO - 3 > CH_3PO_3H_2 > H_3PO_4$

$CF_3S^- < CH_3S^- < OH^-$

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16.9: Lewis Acids and Bases

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented. 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. The Brønsted–Lowry concept of acids and bases defines a base as any species that can accept a proton, and an acid as any substance that can donate a proton. Lewis proposed an alternative definition that focuses on *pairs of electrons* instead. According to Lewis:

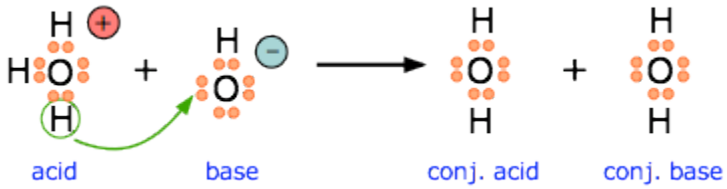
- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

Note

In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.

Lewis Acid-Base Neutralization Involving 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.

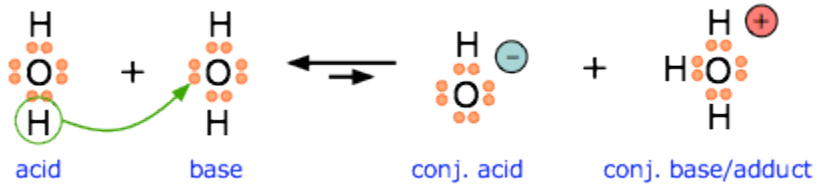


This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

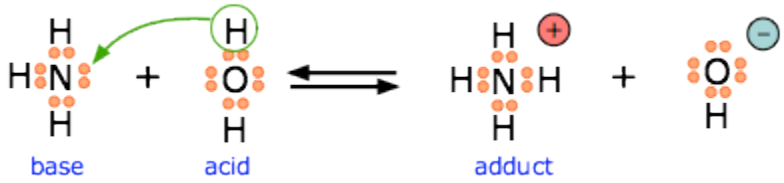
- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* 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.

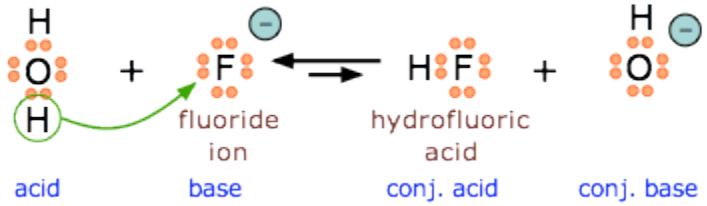
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product 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.



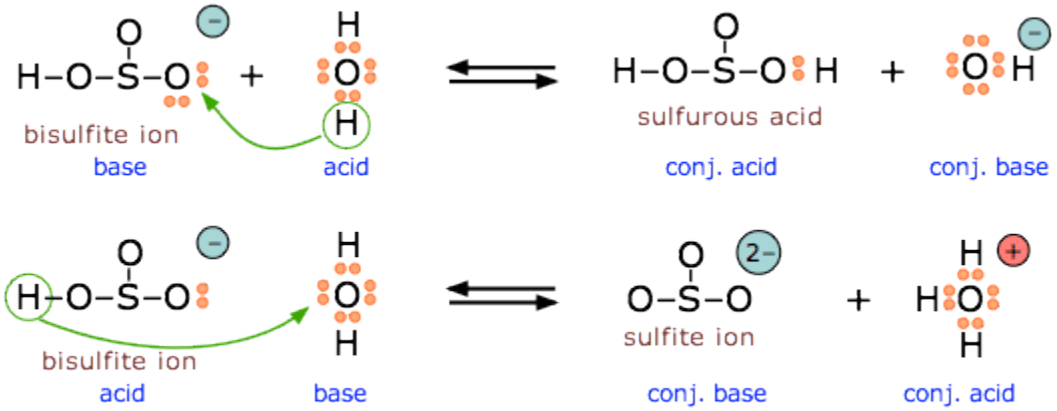
Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.



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.



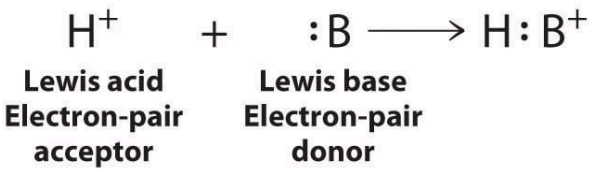
The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.

Note

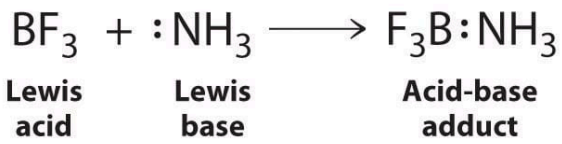
All Brønsted–Lowry bases (proton acceptors), such as OH^-, H_2O, and NH_3, are also electron-pair donors. Thus the Lewis definition of acids and bases does not contradict the Brønsted–Lowry definition. Rather, it expands the definition of acids to include substances other than the H^+ ion.

Lewis Acid-Base Neutralization without Transferring Protons

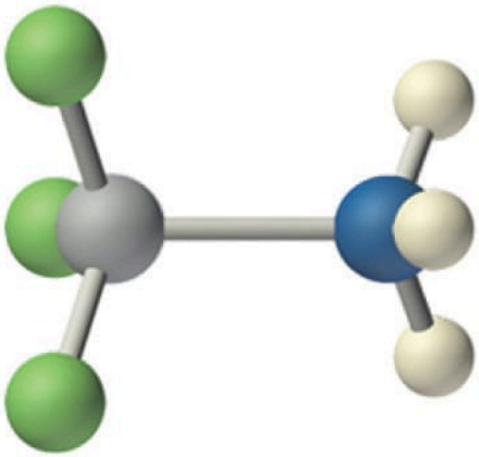
Electron-deficient molecules, such as BCl_3, contain less than an octet of electrons around one atom and have a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. Lewis's definition, which is less restrictive than either the Brønsted–Lowry or the Arrhenius definition, grew out of his observation of this tendency. A general Brønsted–Lowry acid–base reaction can be depicted in Lewis electron symbols as follows:



The proton (H^+), which has no valence electrons, is a Lewis acid because it accepts a lone pair of electrons on the base to form a bond. The proton, however, is just one of many electron-deficient species that are known to react with bases. For example, neutral compounds of boron, aluminum, and the other Group 13 elements, which possess only six valence electrons, have a very strong tendency to gain an additional electron pair. Such compounds are therefore potent Lewis acids that react with an electron-pair donor such as ammonia to form an acid–base adduct, a new covalent bond, as shown here for boron trifluoride (BF_3):



The bond formed between a Lewis acid and a Lewis base is a *coordinate covalent bond* because both electrons are provided by only one of the atoms (N, in the case of $F_3B{:}NH_3$). After it is formed, however, a coordinate covalent bond behaves like any other covalent single bond.



Boron trifluoride-ammonia adduct

Species that are very weak Brønsted–Lowry bases can be relatively strong Lewis bases. For example, many of the group 13 trihalides are highly soluble in ethers (R–O–R′) because the oxygen atom in the ether contains two lone pairs of electrons, just as in H_2O. Hence the predominant species in solutions of electron-deficient trihalides in ether solvents is a Lewis acid–base adduct. A reaction of this type is shown in Figure 16.9.1 for boron trichloride and diethyl ether:

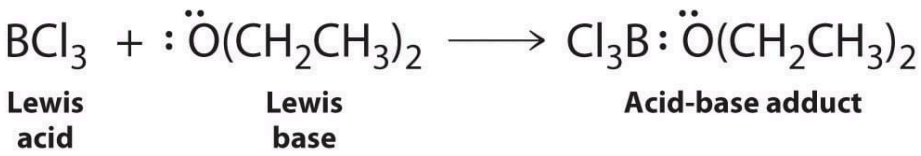
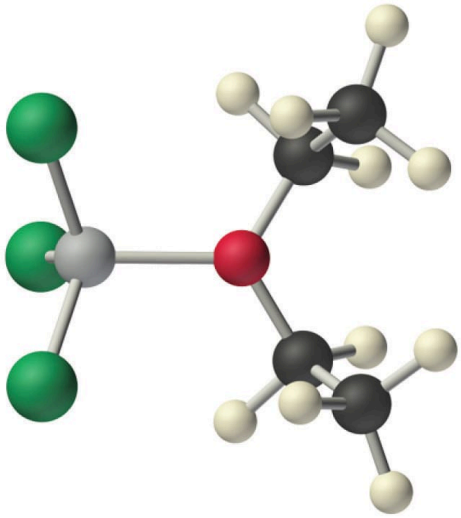


Figure 16.9.1: *Lewis Acid/Base reaction of boron trichloride and diethyl ether reaction*

Note

- Electron-deficient molecules (those with less than an octet of electrons) are Lewis acids.
- The acid-base behavior of many compounds can be explained by their Lewis electron structures.

Many molecules with multiple bonds can act as Lewis acids. In these cases, the Lewis base typically donates a pair of electrons to form a bond to the central atom of the molecule, while a pair of electrons displaced from the multiple bond becomes a lone pair on a terminal atom.



Boron trichloride-diethyl ether adduct

Figure 16.9.2. The highly electronegative oxygen atoms pull electron density away from carbon, so the carbon atom acts as a Lewis acid. Arrows indicate the direction of electron flow.

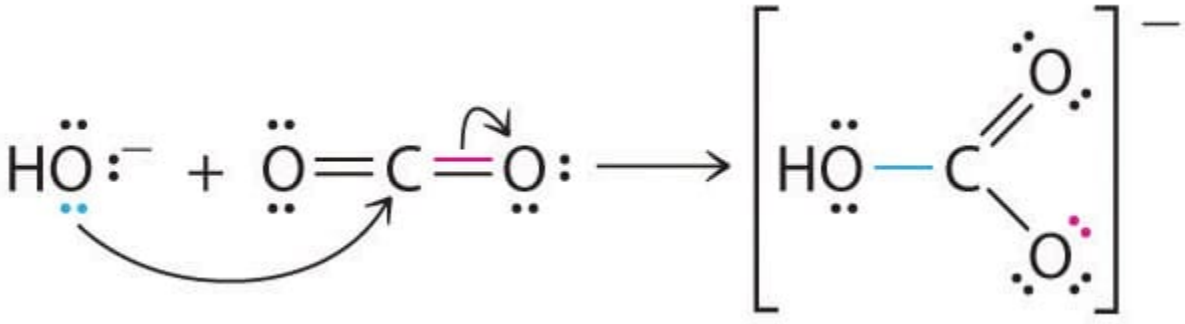


Figure 16.9.2: *Lewis Acid/Base reaction of the hydroxide ion with carbon dioxide*

Example 16.9.1

Identify the acid and the base in each Lewis acid–base reaction.

a. $BH_3 + (CH_3)_2S \rightarrow H_3B{:}S(CH_3)_2$
b. $CaO + CO_2 \rightarrow CaCO_3$
c. $BeCl_2 + 2\ Cl^- \rightarrow BeCl_4^{2-}$

Given: reactants and products

Asked for: identity of Lewis acid and Lewis base

Strategy:

In each equation, identify the reactant that is electron deficient and the reactant that is an electron-pair donor. The electron-deficient compound is the Lewis acid, whereas the other is the Lewis base.

Solution:

a. In BH_3, boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair. Like oxygen, the sulfur atom in $(CH_3)_2S$ has two lone pairs. Thus $(CH_3)_2S$ donates an electron pair on sulfur to the boron atom of BH_3. The Lewis base is $(CH_3)_2S$, and the Lewis acid is BH_3.

b. As in the reaction shown in Equation 8.21, CO_2 accepts a pair of electrons from the O^{2-} ion in CaO to form the carbonate ion. The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so CO_2 is the Lewis acid.
c. The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to $BeCl_2$, which has only four electrons around Be. Thus the chloride ions are Lewis bases, and $BeCl_2$ is the Lewis acid.

Exercise 16.9.1

Identify the acid and the base in each Lewis acid–base reaction.

a. $(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O{:}BF_3$
b. $H_2O + SO_3 \rightarrow H_2SO_4$

Answer

a. Lewis base: $(CH_3)_2O$; Lewis acid: BF_3
b. Lewis base: H_2O; Lewis acid: SO_3

Exercise 16.9.2

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. $Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $[Ni^{2+} + 6NH_3 \rightarrow Ni(NH_3)_5^{2+}$

Non-Aqueous 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 16.9.1). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The limiting acid in a given solvent is the solvonium ion, such as H_3O^+ (hydronium) ion in water. An acid which has more of a tendency to donate a hydrogen ion than the limiting acid will be a strong acid in the solvent considered, and will exist mostly or entirely in its dissociated form. Likewise, the limiting base in a given solvent is the solvate ion, such as OH^- (hydroxide) ion, in water. A base which has more affinity for protons than the limiting base cannot exist in solution, as it will react with the solvent.

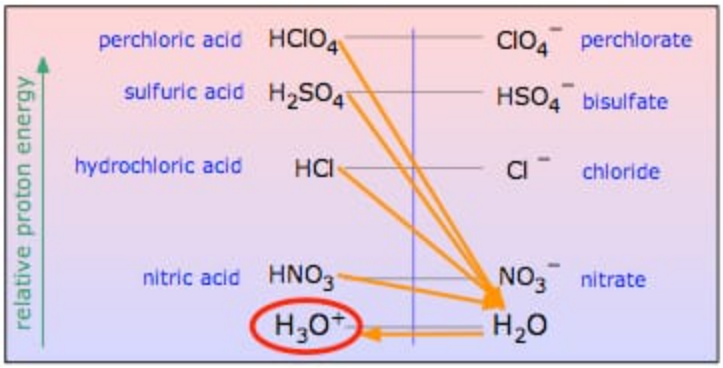


Figure } {16{.}9{.}\eatSpaces{3} \endSpaces}\): *Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling effect" of the solvent.*

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. Bases can exist in solution in liquid ammonia which cannot exist in aqueous solution: this is the case for any base which is **stronger** than the hydroxide ion, but **weaker** than the amide ion NH_2^-. The limiting acid in liquid ammonia is the ammonium ion, which has a pK_a value in water of 9.25. The limiting base is the amide ion, NH_2^-. This is a stronger base than the hydroxide ion and so cannot exist in aqueous solution. The pK_a value of ammonia is estimated to be approximately 33. Any acid which is a stronger acid than the ammonium ion will be a strong acid in liquid ammonia. This is the case for acetic acid, which is completely dissociated in liquid ammonia solution. The addition of pure acetic acid and the addition of ammonium acetate have exactly the same effect on a liquid ammonia solution: the increase in its acidity: in practice, the latter is preferred for safety reasons.

Note

As with OH^- and H_3O^+ in water, the strongest acid and base in NH_3 is dictated by the corresponding autoprotolysis reaction of the solvent:

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

One use of non-aqueous 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. Many familiar substances can serve as the basis of protonic solvent systems (Table 16.9.1).

Table 16.9.1: *Popular Solvent systems*

solvent	autoprotolysis reaction	pK_a
water	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	14
ammonia	$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$	33
acetic acid	$2CH_3COOH \rightleftharpoons CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + C_2H_5O^-$	19
hydrogen peroxide	$2HO-OH \rightleftharpoons HO-OH_2^+ + HO-O^-$	13
hydrofluoric acid	$2HF \rightleftharpoons H^2F^+ + F^-$	10
sulfuric acid	$2H_2SO_4 \rightleftharpoons H3SO_4^+ + HSO_4^-$	3.5

The extreme case is a **superacid**, a medium in which the hydrogen ion is only very weakly solvated. The classic example is a mixture of antimony pentafluoride and liquid hydrogen fluoride:

$$SbF_5 + HF \rightleftharpoons H^+ + SbF_6^- \tag{16.9.1}$$

The limiting base, the hexfluoroantimonate anion SbF_6^-, is so weakly attracted to the hydrogen ion that virtually any other base will bind more strongly: hence, this mixture can be used to protonate organic molecules which would not be considered bases in other solvents. It should noted that pH is undefined in aprotic solvents, which assumes presence of hydronium ions. In other solvents, the concentration of the respective solvonium/solvate ions should be used (e.g., $[NH_4^+]$ and $[NH_2^-]$ in $NH_{3(l)}$.

Contributors and Attributions

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17: ADDITIONAL ASPECTS OF ACID-BASE EQUILIBRIA

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

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17.1: Common-Ion Effect in Acid-Base Equilibria

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:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 && (17.1.2)\\ &= s \times (2s)^2 && (17.1.3)\\ 1.7 \times 10^{-5} &= 4s^3 && (17.1.4)\\ s^3 &= \frac{1.7 \times 10^{-5}}{4} && (17.1.5)\\ &= 4.25 \times 10^{-6} && (17.1.6)\\ s &= \sqrt[3]{4.25 \times 10^{-6}} && (17.1.7)\\ &= 1.62 \times 10^{-2}\ mol\ dm^{-3} && (17.1.8)\end{aligned}$$

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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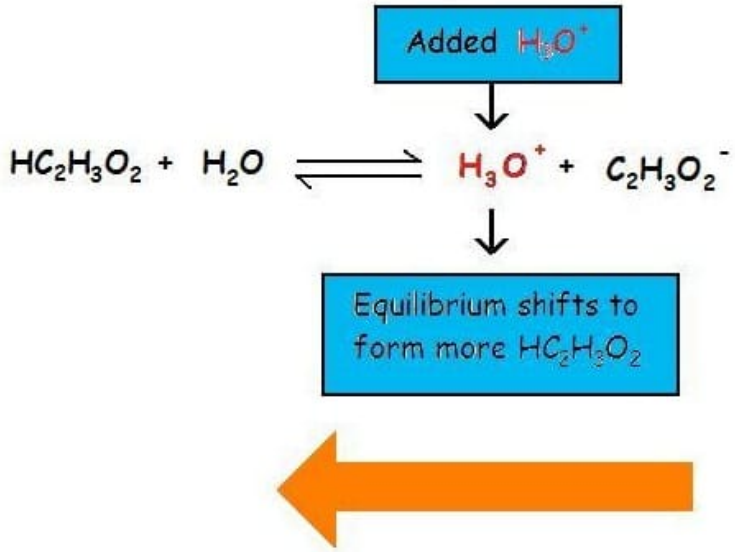
A Video Discussing Finding the Solubility of a Salt: Finding the Solubility of a Salt(opens in new window) [youtu.be]

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.

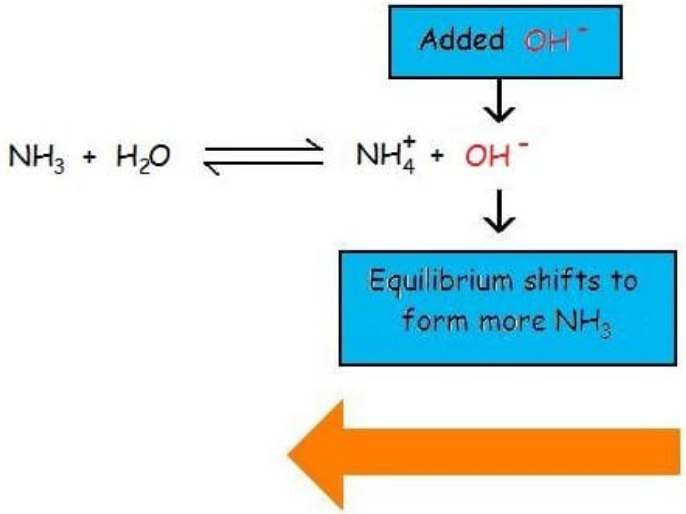
The common ion effect of H_3O^+ on the ionization of acetic acid



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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References

1. Harwood, William S., F. G. Herring, Jeffry D. Madura, and Ralph H. Petrucci. General Chemistry Principles and Modern Applications. 9th ed. New Jersey: Prentice Hall, 2007.

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17.2: Buffer 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 $\mathrm{H^+}$). 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:

$$\mathrm{CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)} \tag{17.2.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[\mathrm{H^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3CO_2H}]} \tag{17.2.2}$$

Sodium acetate ($\mathrm{CH_3CO_2Na}$) is a strong electrolyte that ionizes completely in aqueous solution to produce $\mathrm{Na^+}$ and $\mathrm{CH_3CO_2^-}$ 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 $\mathrm{CH_3COO^-}$ and some of the $\mathrm{H^+}$ ions originally present in solution.

Because $\mathrm{Na^+}$ 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 $[\mathrm{H^+}]$ is less than the initial value. Because $[\mathrm{H^+}]$ 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, $[\mathrm{H^+}]$ increases. Once again the equilibrium is temporarily disturbed, but the excess $\mathrm{H^+}$ ions react with the conjugate base ($\mathrm{CH_3CO_2^-}$), 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 [$\mathrm{CH_3CO_2^-}$] 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 $\mathrm{CH_3CO_2^-}$, 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.

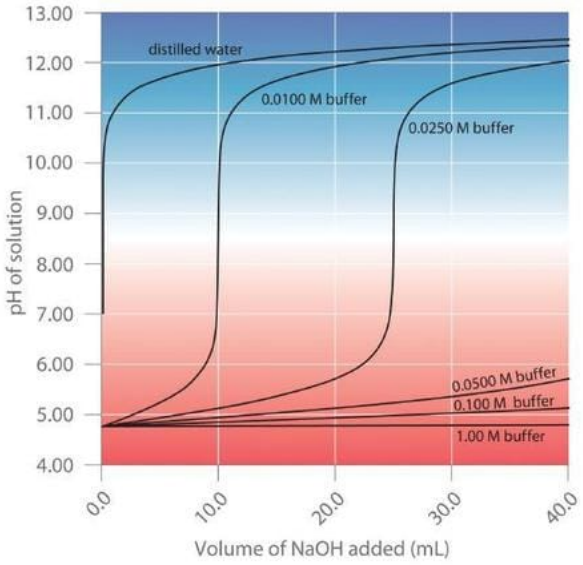


Figure 17.2.1: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)
Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

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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The Change in pH with the Addition of a Strong Base to a Buffer:

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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.

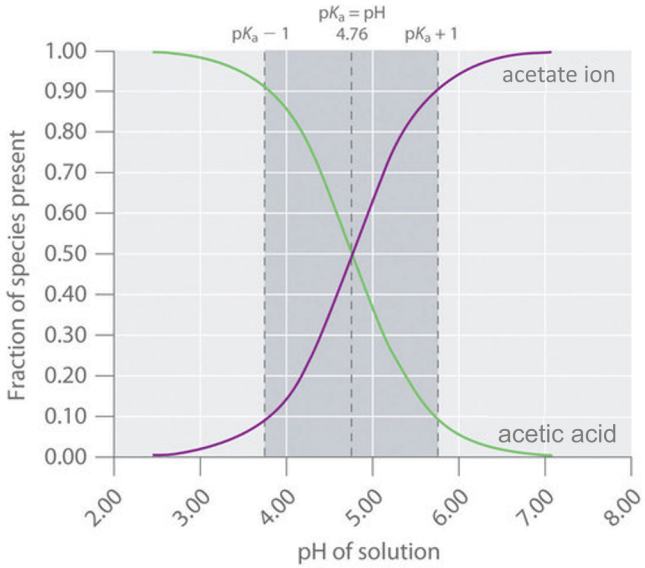


Figure 17.2.2: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable 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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A Video Discussing The Buffer Region: The Buffer Region (opens in new window) [youtu.be]

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.

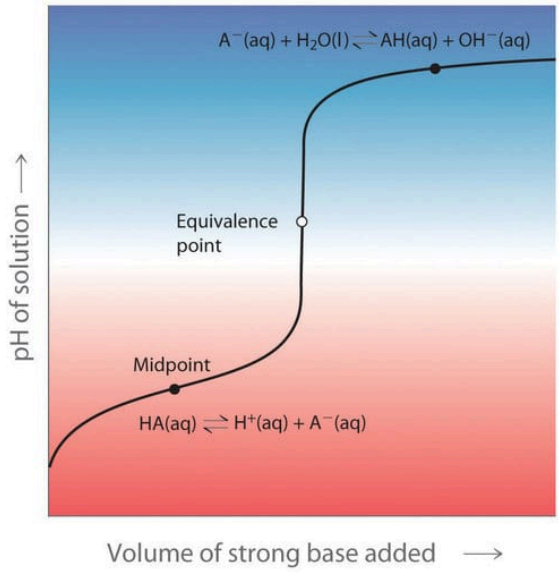


Figure 17.2.3: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)

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.

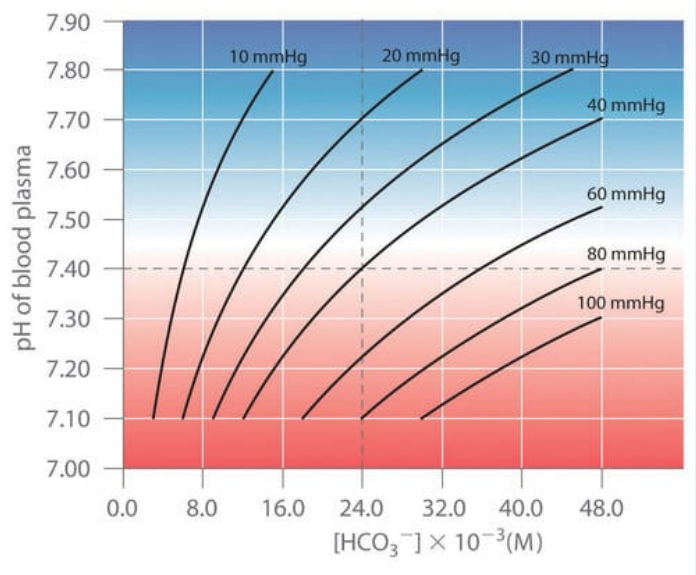


Figure 17.2.4: Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of P_{CO_2}. Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated 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 Indicators

Learning Objectives

- Explain the function and color changes of acid-base indicators
- Demonstrate how to select the proper indicator for a titration experiment
- Determine the acidic dissociation constants K_a or K_{ai} of indicators.

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than 5.0×10^{-9} *M* (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0×10^{-9} *M* (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called acid-base indicators. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$\underbrace{\mathrm{HIn}_{(aq)}}_{\text{red}} + \mathrm{H_2O}_{(l)} \rightleftharpoons \mathrm{H_3O^+}_{(aq)} + \underbrace{\mathrm{In^-}_{(aq)}}_{\text{yellow}} \tag{17.3.1}$$

$$K_a = \frac{[H3O+][In-]}{[HIn]} = 4.0 \times 10^{-4} \tag{17.3.2}$$

The anion of methyl orange, In^-, is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

An indicator's color is the visible result of the ratio of the concentrations of the two species In^- and HIn. If most of the indicator (typically about 60–90% or more) is present as In^-, then we see the color of the In^- ion, which would be yellow for methyl orange. If most is present as HIn, then we see the color of the HIn molecule: red for methyl orange. For methyl orange, we can rearrange the equation for K_a and write:

$$\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_a}{[\mathrm{H_3O^+}]} \tag{17.3.3}$$

This shows us how the ratio of $\frac{[In-]}{[HIn]}$ varies with the concentration of hydronium ion. The above expression describing the indicator equilibrium can be rearranged:

$$\frac{[\mathrm{H_3O^+}]}{K_a} = \frac{[\mathrm{HIn}]}{[\mathrm{In^-}]} \tag{17.3.4}$$

$$\log\left(\frac{[\mathrm{H_3O^+}]}{K_a}\right) = \log\left(\frac{[\mathrm{HIn}]}{[\mathrm{In^-}]}\right) \tag{17.3.5}$$

$$\log([\mathrm{H_3O^+}]) - \log(K_a) = -\log\left(\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}\right) \tag{17.3.6}$$

$$-\mathrm{pH} + \mathrm{p}K_a = -\log\left(\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}\right) \tag{17.3.7}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}\right) \text{ or } \mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \tag{17.3.8}$$

The last formula is the same as the Henderson-Hasselbalch equation, which can be used to describe the equilibrium of indicators.

When $[H_3O^+]$ has the same numerical value as K_a, the ratio of $[In^-]$ to [HIn] is equal to 1, meaning that 50% of the indicator is present in the red form (HIn) and 50% is in the yellow ionic form (In^-), and the solution appears orange in color. When the hydronium ion concentration increases to 8×10^{-4} *M* (a pH of 3.1), the solution turns red. No change in color is visible for any further increase in the hydronium ion concentration (decrease in pH). At a hydronium ion concentration of 4×10^{-5} *M* (a pH of 4.4), most of the indicator is in the yellow ionic form, and a further decrease in the hydronium ion concentration (increase in pH) does not produce a visible color change. The pH range between 3.1 (red) and 4.4 (yellow) is the color-change interval of methyl orange; the pronounced color change takes place between these pH values.

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 (Figure 17.3.1). In all cases, though, 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 pKin that is within one pH unit of the expected pH at the equivalence point of the titration.



Figure 17.3.1: Naturally Occurring pH Indicators in Red Cabbage Juice. Image curtesty of Wikipedia.

Red cabbage juice contains a mixture of substances whose color depends on the pH. Each test tube contains a solution of red cabbage juice in water, but the pH of the solutions varies from pH = 2.0 (far left) to pH = 11.0 (far right). At pH = 7.0, the solution is blue.

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure 17.3.2 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

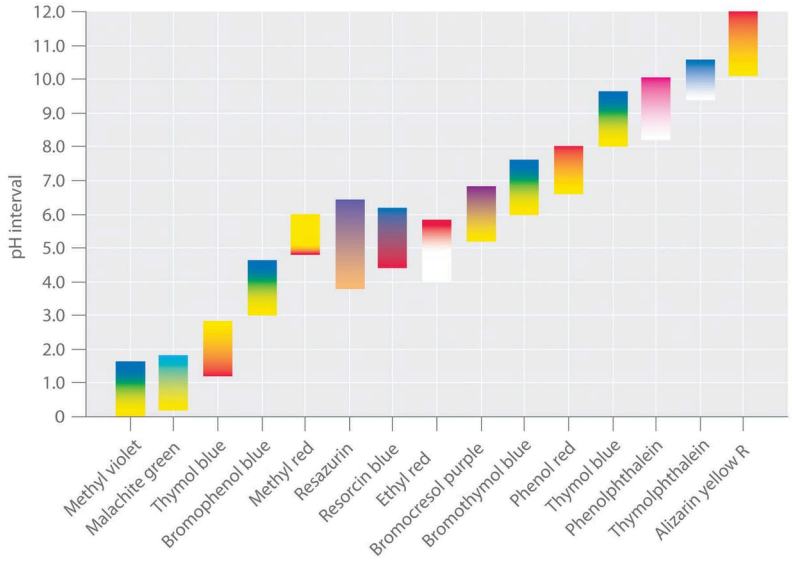


Figure 17.3.2: Some Common Acid–Base Indicators. Approximate colors are shown, along with pKin values and the pH range over which the color changes.

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 in Section 16, 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 17.3.3. 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.

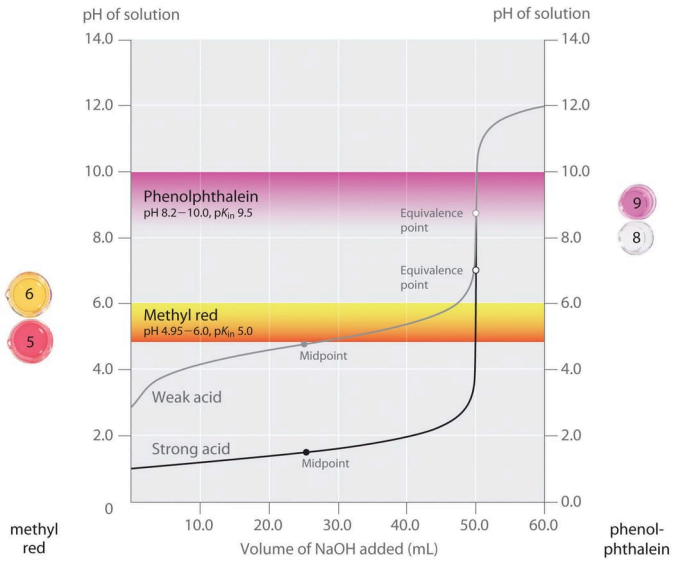


Figure 17.3.3: Choosing the Correct Indicator for an Acid–Base Titration

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 pKa 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 pK in 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.

Example 17.3.1

In the titration of a weak acid with a strong base, which indicator would be the best choice?

a. Methyl Orange
b. Bromocresol Green
c. Phenolphtalein

Solution

The correct answer is C. In the titration of a weak acid with a strong base, the conjugate base of the weak acid will make the pH at the equivalence point greater than 7. Therefore, you would want an indicator to change in that pH range. Both methyl orange and bromocresol green change color in an acidic pH range, while phenolphtalein changes in a basic pH.

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 17.3.4).

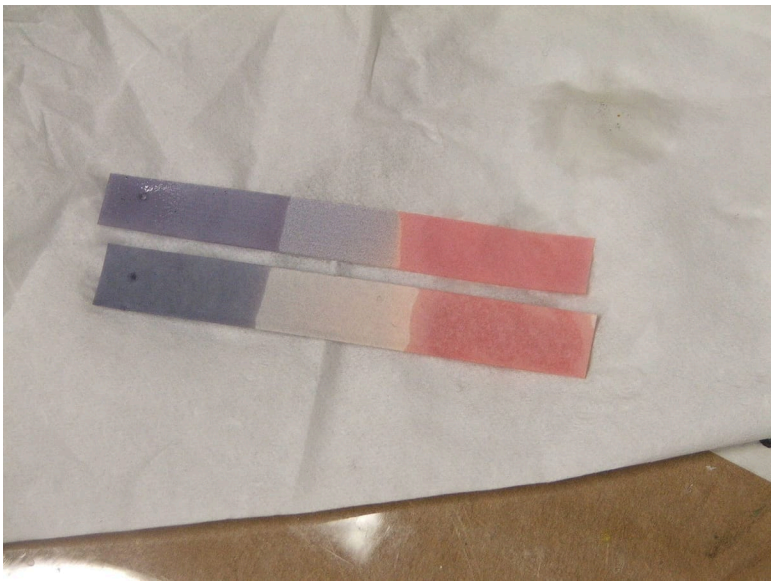


Figure 17.3.4: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided.

YouTube Video

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pH Indicators: https://youtu.be/1IqzUa5lABs

Summary

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.

Contributors and Attributions

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17.4: Neutralization Reactions and Titration Curves

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 $17.4.1a$ 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 $17.4.1b$. 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.

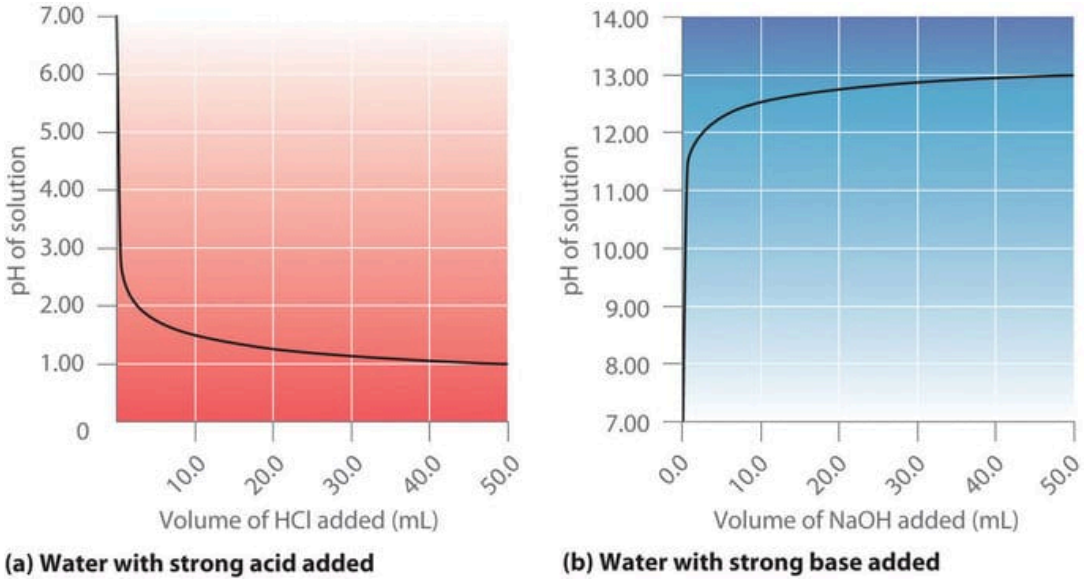


Figure $17.4.1$: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 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 $17.4.2a$):

$$\mathrm{OH^- + H^+ \rightleftharpoons H_2O}.$$

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:

$$moles\ of\ base = (volume)_b(molarity)_b V_b M_b = moles\ of\ acid = (volume)_a(molarity)_a = V_a M_a \tag{17.4.1}$$

If 0.20 M $NaOH$ is added to 50.0 mL of a 0.10 M solution of HCl, we solve for V_b:

$$V_b(0.20Me) = 0.025L = 25mL$$

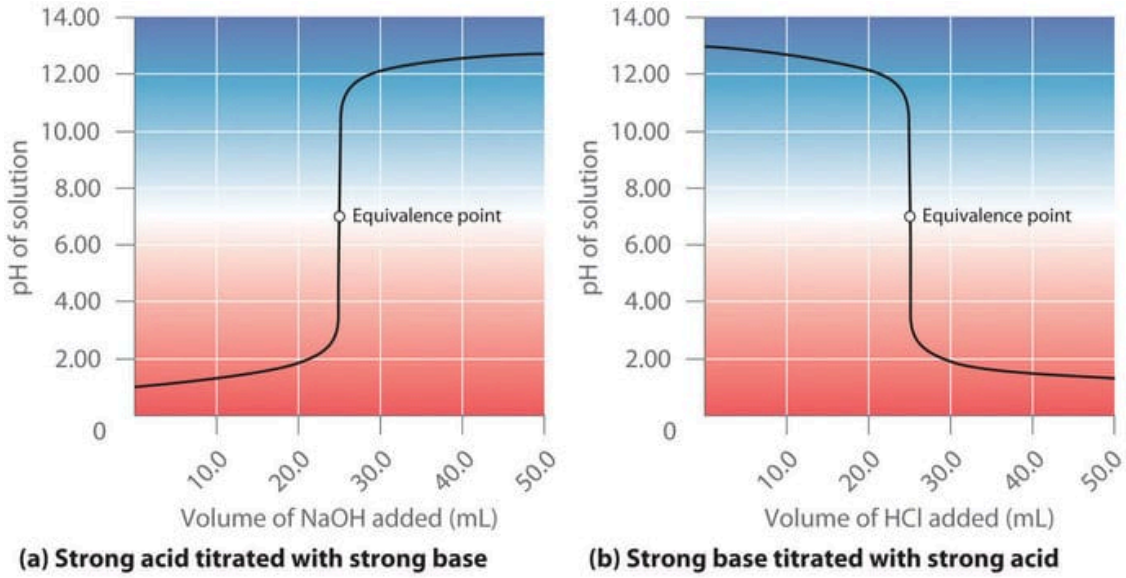


Figure 17.4.2: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M $NaOH$ is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly 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 17.4.2*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 17.4.2*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 17.4.1: 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 17.4.1

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.

YouTube Video

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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 $17.4.3a$ 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 $17.4.2$. 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.

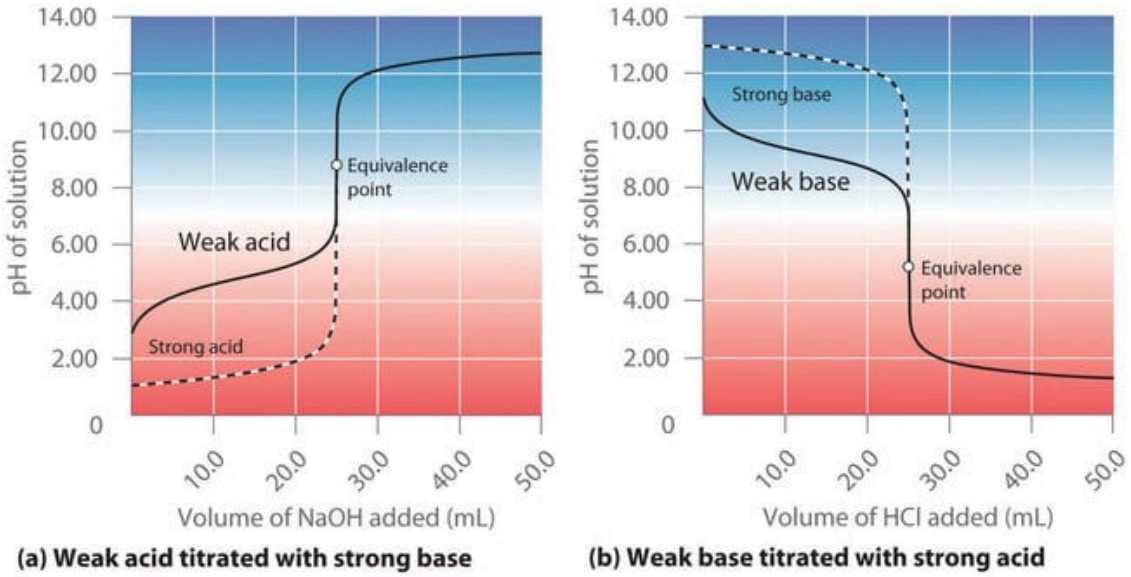


Figure 17.4.3: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more 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 17.4.3a 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 17.4.2 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 17.4.3). 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:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{17.4.2}$$

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 $17.4.3a$, 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 $17.4.2$, 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 17.4.2

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 $\mathrm{OH^-}$, 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

$$K_b = \frac{K_w}{K_a} \tag{17.4.3}$$

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 17.4.3:

$$K_b = \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.80 \times 10^{-10} \tag{17.4.4}$$

Substituting the expressions for the final values from the ICE table into Equation 17.4.4 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 17.4.3a). 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 17.4.2

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 17.4.3, 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 $17.4.4$ 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.

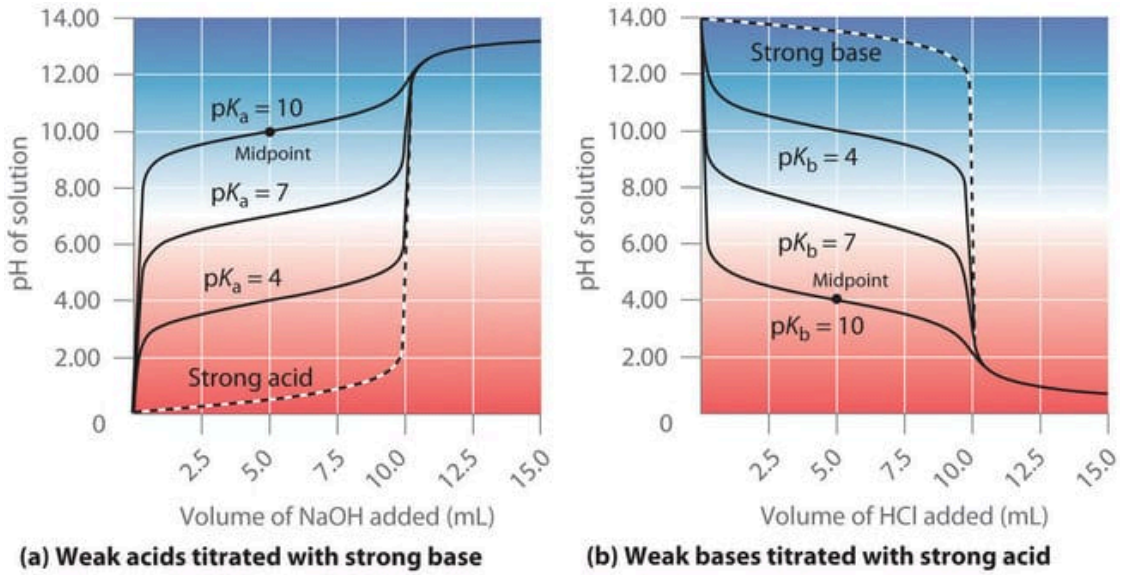


Figure $17.4.4$: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added 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 $17.4.4a$ and $17.4.4b$ 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

$$pK_a = pH \tag{17.4.5}$$

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 $17.4.4$ 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 $17.4.5$ 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.

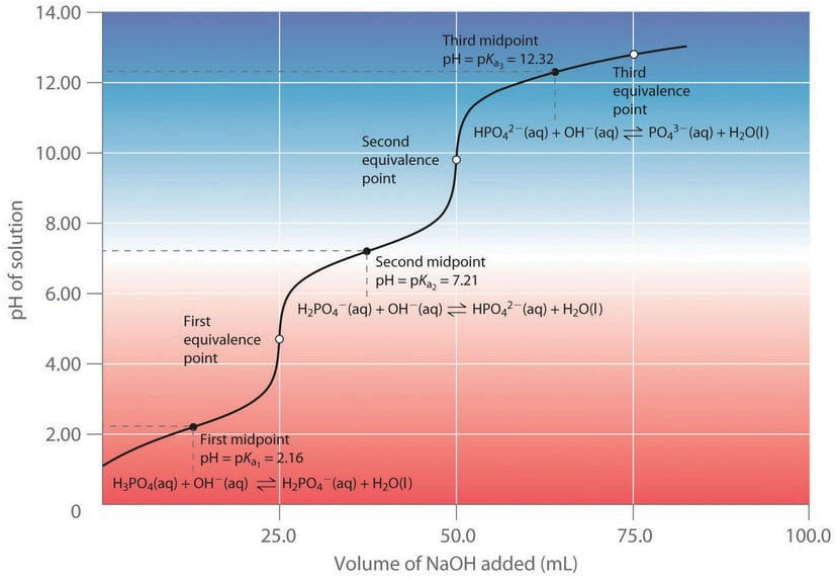
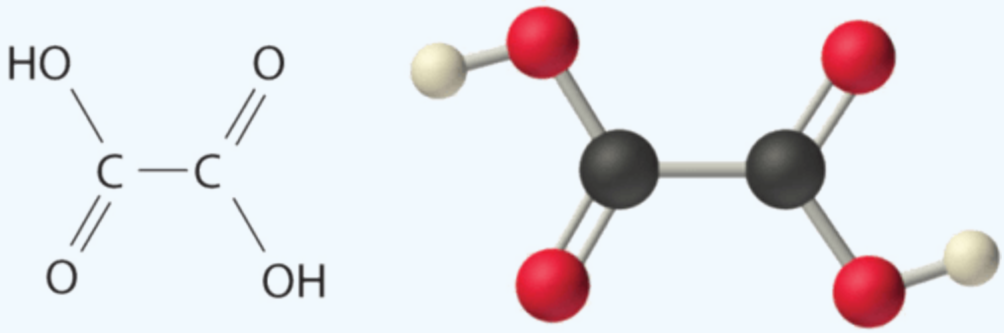


Figure $17.4.5$: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation 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 $17.4.5$. 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 17.4.3

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 17.4.2:

$$\text{final volume of solution} = 100.0\,mL + 55.0\,mL = 155.0\,mL$$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$[Hox^-] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$\left[ox^{2-}\right] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2} = \frac{\left[ox^{2-}\right][H^+]}{[Hox^-]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$[H^+] = \frac{K_{a2}\,[Hox^-]}{\left[ox^{2-}\right]} = \frac{\left(1.6 \times 10^{-4}\right)\left(2.32 \times 10^{-2}\right)}{\left(9.68 \times 10^{-3}\right)} = 3.7 \times 10^{-4}\ M$$

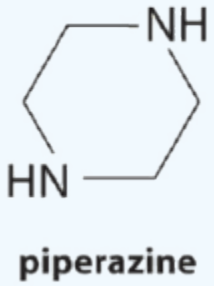
So

$$pH = -\log\left[H^+\right] = -\log\left(3.7 \times 10^{-4}\right) = 3.43$$

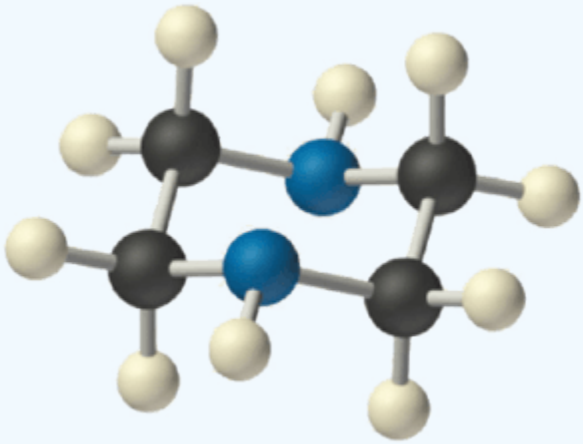
This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}), but we added only enough to titrate less than 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 17.4.3: 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:

$$K_{In} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \tag{17.4.6}$$

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 $17.4.6$). 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 $17.4.6$: 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 $17.4.7$ 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

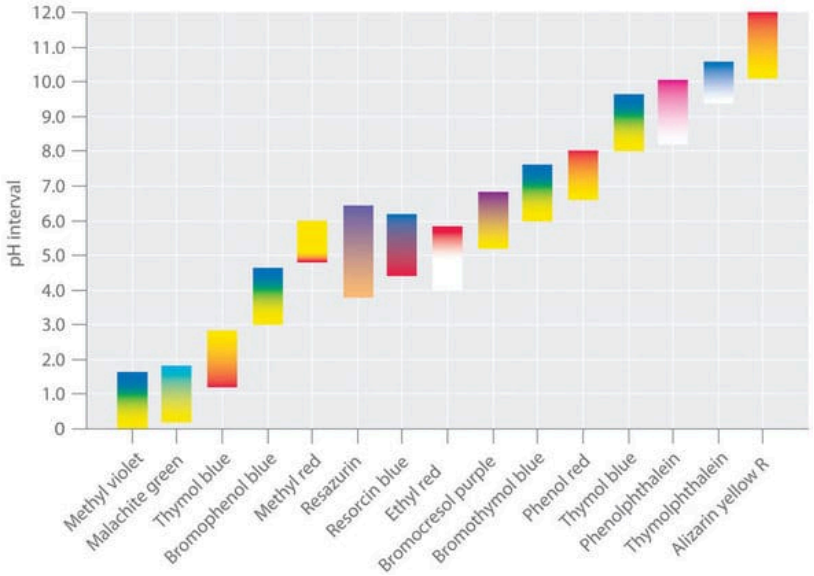


Figure 17.4.7: Some Common Acid–Base Indicators. Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

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 17.4.8. 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.

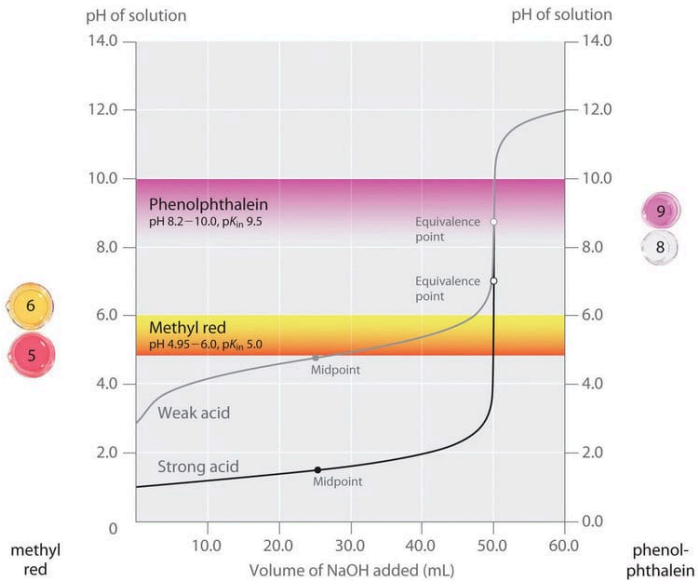


Figure 17.4.8: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

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 17.4.9).

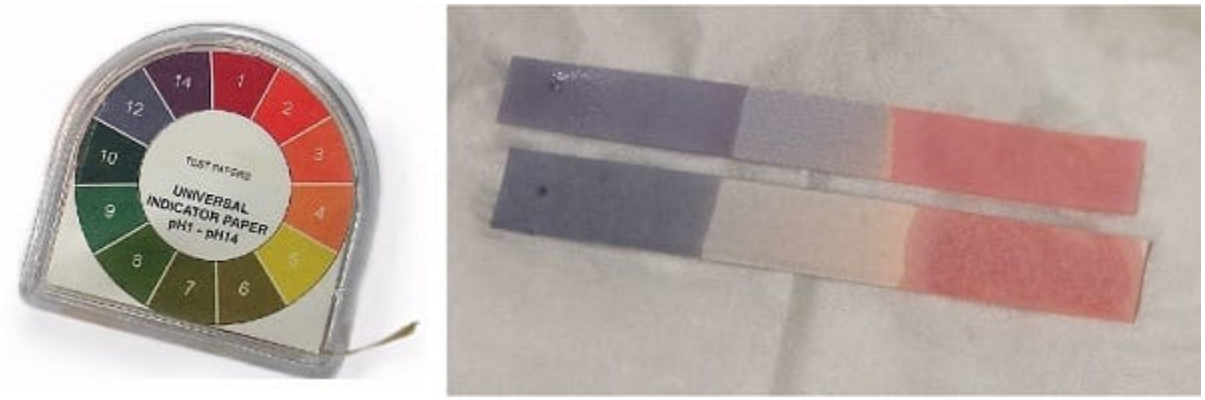


Figure 17.4.9: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)

YouTube Video

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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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 17.4.1

11.6

Exercise 17.4.2

9.23

Exercise 17.4.3**: Piperazine**

pH=4.9

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17.5: Solutions of Salts of Polyprotic Acids

Learning Objectives

- Predict and calculate the pH of a solution of salts of polyprotic acids

Salts can be thought of as being derived from the neutralization of an acid and a base. A salt formed from a strong acid and a strong base will not hydrolyze (e.g., extract a proton from water). When placed in water, these salts dissociate completely, and their ions remain uncombined in solution (e.g., the NaCl salt is formed from a strong acid (HCl) and a strong base (NaOH).

In discussing the titration of acids and bases, the acid or basic properties of the corresponding salts after a neutralization reaction must be addressed to calculate the final pH of a solution. To calculate the pH of a salt solution one needs to know the concentration of the salt solution, whether the salt is an acidic, basic, or neutral salt, the equation for the interaction of the ion with the water, the equilibrium expression for this interaction and the K_a or K_b value.

Note: The Hydrolysis of Salts

As a quick review, the general rules for the hydrolysis of monoprotic salts are:

1. If neither the cation/anion can affect the pH, the solution is neutral
2. If **only** the cation of the salt is acidic, the solution is acidic
3. If **only** the anion of the salt is basic, the solution will be basic
4. If a salt has a cation that is acidic and an anion that is basic, the pH of the solution is determined by the relative strengths of the acid and base
    - if $K_a = K_b$, then no net effect on pH
    - if $K_a > K_b$, then the solution is slightly acidic
    - if $K_b > K_b$, then the solution is slightly basic

Salts of Polyprotic Acids

Do not be intimidated by the salts of polyprotic acids. Yes they're bigger and "badder" then most other salts, but they can be handled the exact same way as other salts, just with a bit more math.

- All of the rules from above still apply, e.g., the pH of a salt of polyprotic acid will always be greater than 7.
- The same way that polyprotic acids lose H^+ stepwise, salts of polyprotic acids gain H^+ in the same manner, but in reverse order of the polyprotic acid.

Take for example dissociation of carbonic acid (H_2CO_3):

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO^-_{3(aq)} \tag{17.5.1}$$

with $K_{a1} = 2.5 \times 10^{-4}$

$$HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CO^{2-}_{3(aq)} \tag{17.5.2}$$

with $K_{a2} = 5.61 \times 10^{-11}$. This means that when calculating the values for K_b of CO_3^{2-}, The K_b of the first hydrolysis reaction will be $K_{b1} = \frac{K_w}{K_{a2}}$ since it will go in the reverse order.

Example 17.5.1: $NaHSO_4$

What is the pH of a 0.100 M $\mathrm{NaHSO_4}$ solution? Sulfuric acid is a strong acid, and the $\mathrm{p}K_{\mathrm{a}_2}$ of $\mathrm{HSO_4}^-$ is 1.92.

Solution

First review the ions generates immediate upon dissociation of the salt.

- Na^+ is a non-acidic "spectator ion" that does not affect the acidity or basicity of a solution and can be ignored.
- The HSO_4^- anion will affect the pH

HSO_4^- is part of the dissociation chain of diprotic sulfuric acid (H_2SO_4) with the following steps

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^- \tag{17.5.3}$$

Because H_2SO_4 is a strong acid, this step goes to completion and no H_2SO_4 exists in the solution. The HSO_4^- ion is a weak acid and dissociates to a small extent:

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-} \tag{17.5.4}$$

with $K_{a2} = 1.0 \times 10^{-2}$ from Table E1. The equilibrium favors the reactants.

The $NaHSO4$ salt is completely ionized in its solution.

$$\mathrm{NaHSO_4}_{(s)} \rightarrow \mathrm{Na^+}_{(sq)} + \mathrm{HSO_4^-}_{(sq)} \tag{17.5.5}$$

The anion then further ionizes (Equation 17.5.4). We can construct an ICE table to solve for the final value of this ionization and hence $[H_3O^+]$

ICE Table	HSO_4^-	H_2O	H_3O^+	SO_4^{2-}
Initial	0.1 M	-	0	0
Change	-x	-	+x	+x
Equilibrium	0.1 M -x	-	x	x

$$K_{a2} = \frac{x^2}{0.100 - x} = 0.0100$$

$$\begin{aligned}[\mathrm{H_3O^+}] &= x \\ &= \frac{-0.120 + \sqrt{0.012^2 + 4 \times 0.00120}}{2} \\ &= 0.0292 \text{ M}\end{aligned}$$

Thus,

$$\mathrm{pH} = -\log\ 0.0292 = 1.54$$

Note that while the dissociation is weak, the quadratic equation cannot be avoided since 0.0292 cannot be ignore when compared to 0.1 M.

Exercise 17.5.1

Which of the following solutions are acidic, basic, or neutral?

a. $\mathrm{Na_2SO_4}$
b. $\mathrm{NaH_2PO_4}$

c. Na_2HPO_4
d. Na_3PO_4
e. $NaNO_3$

Example 17.5.2: Qualitatively Estimating the pH of a Polyprotic Salt Solution

Predict whether the Na_2HPO_4 salt will form an acidic or basic solution when dissolved in water. You will need values from Table E1 to address this.

Solution

First review the ions generates immediate upon dissociation of the salt.

- Na^+ is a non-acidic "spectator ion" that does not affect the acidity or basicity of a solution and can be ignored.
- The HPO_4^{2-} anion will affect the pH and does so via competing hydrolysis steps as discussed below.

From Table E1, the three equilibria values for the three acid/base reactions of the phosphate ion are:

$$H_3PO_{4(sq)} \rightleftharpoons H^+_{(aq)} + H_2PO^{2-}_{4(aq)} \tag{17.5.6}$$

with $K_{a1} = 6.9 \times 10^{-3}$

$$H_2PO^-_{4(sq)} \rightleftharpoons H^+_{(aq)} + HPO^{2-}_{4(aq)} \tag{17.5.7}$$

with $K_{a2} = 6.2 \times 10^{-8}$

$$HPO^{2-}_{4(sq)} \rightleftharpoons H^+_{(aq)} + PO^{3-}_{4(aq)} \tag{17.5.8}$$

with $K_{a3} = 4.8 \times 10^{-11}$

The low K_a value for the deprotonation of $HPO^{2-}_{4(sq)}$ means that it is a poor acid and better functions as a (Brønsted-Lowry) base:

$$HPO^{2-}_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_2PO^-_{4(aq)} + OH^-_{(aq)} \tag{17.5.9}$$

The two possible reactions that $HPO^{2-}_{4(aq)}$ undergoes are the acid reaction in Equation 17.5.7 and the basic reaction in Equation 17.5.9. Whether this ion will cause the solution to be acidic or basic depends on whether the K_a for Equation 17.5.7 is bigger than the K_b for Equation 17.5.9.

The K_b of this reaction is related to the K_{a2} by

$$K_b = \frac{K_w}{K_a}$$

$$K_b = \frac{1 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7} \text{ for } HPO_4^{2-}$$

Since $K_b > K_a$, the solution will be **basic**. To determine just how basic requires the use of an ICE table as discussed in Example 17.5.3.

Solving the final pH for a Na_2HPO_4 salt solution is more complex than for the $NaHSO_4$, since the latter involves a single equilibrium. Two equilibria must be simultaneously solved for Na_2HPO_4. However, often time (but not always), they can be easily approximated given the relative pk_a describing the reversible reaction.

Example 17.5.3: Quantitatively Estimating the pH of a Polyprotic Salt Solution

Calculate the pH of the solution containing 3.875 g of Na_2HPO_4 that has been dissolved in a 250 mL of water.

Solution

First it is best to identify the molarity of Na_2HPO_4 that was initially generated (i.e., before any hydrolysis reactions happens).

$$c = \frac{3.875\ g/\text{molecular mass}}{\text{volume}} = \frac{3.875\ g/141.98\ g/mol}{250\ mL} = 0.11\ M$$

As discussed in Example 17.5.1, the low K_a value for the deprotonation of $HPO^{2-}_{4(sq)}$ means that it is a poor acid and instead functions as a base instead. From comparing the ionization constant in Example 17.5.1, the Na_2HPO_4 is a far better base than acid. If we ignore the acid properties of the ion and focus on the basic we get the following reaction

$$HPO^{2-}_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_2PO^{-}_{4(aq)} + OH^{-}_{(aq)} \tag{17.5.10}$$

with a K_b of 1.6×10^{-7}. Now do an ICE table to get the final $[H^+]$ concentration.

ICE Table	$HPO^{2-}_{4(aq)}$	$H_2O_{(l)}$	$H_2PO^{-}_{4(aq)}$	$OH^{-}_{(aq)}$
Initial	0.11 M	-	-	0
Change	-x	-	+x	+x
Equilibrium	0.11 M - x	-	x	x

$$K_b = \frac{[H_2PO^{-}_{4(aq)}][OH^{-}_{(aq)}]}{[HPO^{2-}_{4(aq)}]} = 1.6 \times 10^{-7} \tag{17.5.11}$$

$$\frac{x^2}{0.11\ M - x} = 1.6 \times 10^{-7} \tag{17.5.12}$$

if $x << 0.11\ \ M$ then $0.11\ \ M - x \approx 0.11\ \ M$ then

$$x = 1.3 \times 10^{-4} = [OH^-] \tag{17.5.13}$$

$$pOH = -\log_{10}[OH^-] = 3.8 \tag{17.5.14}$$

\[pH = pK_w - pOH]

Assuming that the reaction is at 25°, then $pK_w = 14$ and

$$pH = 14 - 3.8 = 10.2 \tag{17.5.15}$$

As expected, the solution is basic.

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17.6: Acid-Base Equilibrium Calculations: A Summary

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17.E: Exercises

17.1: Common-Ion Effect in Acid-Base Equilibria

Questions

1. The solubility product K_{sp} for bismuth sulfide Bi_2S_3 is 1.6×10^{-72} at 25 °C. What is the molar solubility of bismuth sulfide in a solution that is 0.0010 M in sodium sulfide Na_2S?
2. John poured 1.0 mL of 0.10 M $NaCl$, 1.0 mL of 0.10 M KOH, and 1.0 mL 0.20 HCl solutions together and then he made the total volume to be 100.0 mL. What is the $[Cl^-]$ in the final solution?
3. The K_{sp} for $AgCl$ is 1.0×10^{-10}. From which of the following solutions would silver chloride precipitate?
   A: A solution 0.10 M in Ag^+ and 1.00 M in Cl^-
   B: A solution $1.0 \times 10^{-5}\ M$ in Ag^+ and 0.20 M in Cl^-
   C: A solution $1.0 \times 10^{-7}\ M$ in Ag^+ and 1.0E-7 M in Cl^-
   a. A only
   b. B only
   c. C only
   d. A and B
   e. A, B, and C

Substance	K_{sp}
magnesium hydroxide	1.2×10^{-11}
magnesium carbonate	1.6×10^{-5}
magnesium fluoride	6.4×10^{-9}

4. Addition of which of the following substances will cause the precipitation of a salt from one liter of a $1 \times 10^{-4}\ M\ Mg^{2+}$ solution?
   a. 1×10^{-4} mole NaOH
   b. 1×10^{-1} mole nitric acid
   c. 1×10^{-5} mole potassium acetate
   d. 1×10^{-4} mole ammonium nitrate
   e. 1×10^{-2} mole sodium fluoride
5. The K_{sp} for strontium chromate is 3.6×10^{-5} and 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 0.10 M solution of barium and strontium ions without precipitating the other?
6. Iron(II) hydroxide is only sparingly soluble in water at 25 °C; its K_{sp} is equal to 7.9×10^{-16}. Calculate the solubility of iron(II) hydroxide in a solution of pH 6.0.

Solutions

1. ***Answer*** 1.08e-13
   Consider...
   x = molar solubility; $(2x)^2\ (0.0010 + 3x)^3 = K_{sp}$; x = ?
2. ***Answer*** 0.0030 M
   Consider...
   Evaluate $[Na^+]$, $[K^+]$, $[H^+]$ and $[OH^-]$ for fun!
3. ***Answer*** d.
   Consider...
   Calculate the $[Ag^+]\ [Cl^-]$ for A, B, and C, and compare their values with K_{sp}.
4. ***Answer*** e.
   Consider...

A lot of calculations to figure out, but it's a common ion problem.

5. ***Answer*** 3.6e-4
   Consider...
   This problem requires some thinking.
6. ***Answer*** 7.9 M
   Consider...
   $[\mathrm{OH^-}]$ = $10^{(-14+6)}$ = 1e-8. x * (1e-8 + x)^2 = K_{sp}; x = ?

17.2: Buffer Solutions

17.3: Acid-Base Indicators

Q17.3.1

There are numerous natural indicators present in plants. The dye in red cabbage, the purple color of grapes, even the color of some flowers are some examples. What is the cause for some fruits to change color when they ripen?

S17.3.1

$[\mathrm{H^+}]$ of the juice changes. The changes in pH or $[\mathrm{H^+}]$ cause the dye to change color if their conjugate acid-base pairs have different colors. There may be other reasons too. Do colors indicate how good or bad they taste?

Q17.3.2

Choose the true statement:

a. All weak acids are indicators.
b. All weak bases are indicators.
c. Weak acids and bases are indicators.
d. All indicators are weak acids.
e. An acid-base conjugate pair has different colors.
f. Any indicator changes color when the pH of its solution is 7.

S17.3.2

d. Color change is a requirement for indicators.

Q17.3.3

Do all indicators change color at pH 7 (y/n)?

S17.3.3

No! Phenolphthalein changes color at pH ~9. Bromothymol blue has a pK_n value of 7.1. At pH 7, its color changes from yellow to blue. Some indicators change color at pH other than 7.

17.4: Neutralization Reactions and Titration Curves

17.5: Solutions of Salts of Polyprotic Acids

17.6: Acid-Base Equilibrium Calculations: A Summary

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18: SOLUBILITY AND COMPLEX-ION EQUILIBRIA

Petrucci: ***General Chemistry***
Principles and Modern Applications

Template:HideTOC

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18.1: Solubility Product Constant, Ksp

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:

$$\mathrm{Ca_3(PO_4)_2\,(s) \rightleftharpoons 3\,Ca^{2+}\,(aq) + 2\,PO_4^{3-}\,(aq)} \tag{18.1.1}$$

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

$$K = \frac{[\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2}{[\mathrm{Ca_3(PO_4)_2}]} \tag{18.1.2}$$

$$[\mathrm{Ca_3(PO_4)_2}]K = K_{sp} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2 \tag{18.1.3}$$

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 18.1.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 18.1.2 and 18.1.3, changes in pH can affect the solubility of a compound as discussed later.

Note

As with K, the concentration of a pure solid does not appear explicitly in K_{sp}.

Table 18.1.1: Solubility Products for Selected Ionic Substances at 25°C

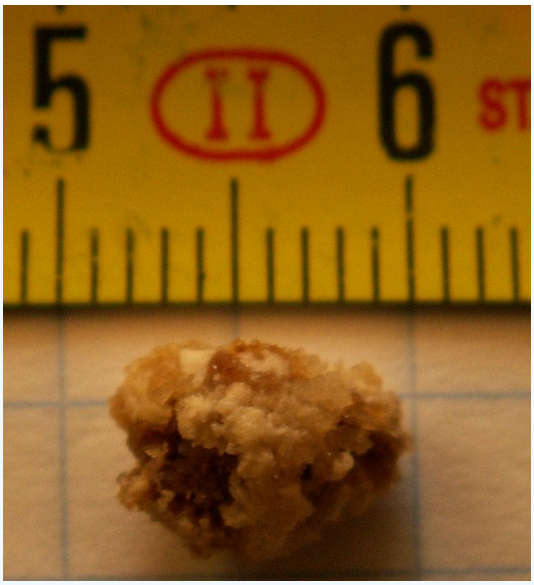
Solid	Color	K_{sp}		Solid	Color	K_{sp}
Acetates				**Iodides**		
$Ca(O_2CCH_3)_2{\cdot}3H_2O$	white	4×10^{-3}		Hg_2I_2*	yellow	5.2×10^{-29}
Bromides				PbI_2	yellow	9.8×10^{-9}
***These contain the Hg_2^{2+} ion.**						

Solid	Color	K_{sp}		Solid	Color	K_{sp}
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}
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.**						

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.

Example 18.1.1

Calcium oxalate monohydrate [$Ca(O_2CCO_2) \cdot H_2O$, also written as $CaC_2O_4 \cdot H_2O$] 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}.



A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2)\cdot H_2O$ and $Ca_3(PO_4)_2$. (Public Doman; Robert R. Wal via Wikipedia).

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:

$$\mathrm{Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {}^{-}O_2CCO_2^{-}(aq) + H_2O(l)} \qquad K_{sp} = [Ca^{2+}][ox^{2-}]$$

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:

$$\frac{7.36 \times 10^{-4}\ \mathrm{g}}{146.1\ \mathrm{g/mol}} = 5.04 \times 10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2)\cdot H_2O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \text{mol Ca}(O_2CCO_2\cdot)H_2O}{100\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1.00\ \text{L}}\right) = 5.04 \times 10^{-5}\ \text{mol/L} = 5.04 \times 10^{-5}\ \text{M}$$

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,

$$\begin{aligned} K_{sp} &= [Ca^{2+}][ox^{2-}] \\ &= (5.04 \times 10^{-5})(5.04 \times 10^{-5}) \\ &= 2.54 \times 10^{-9} \end{aligned}$$

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.

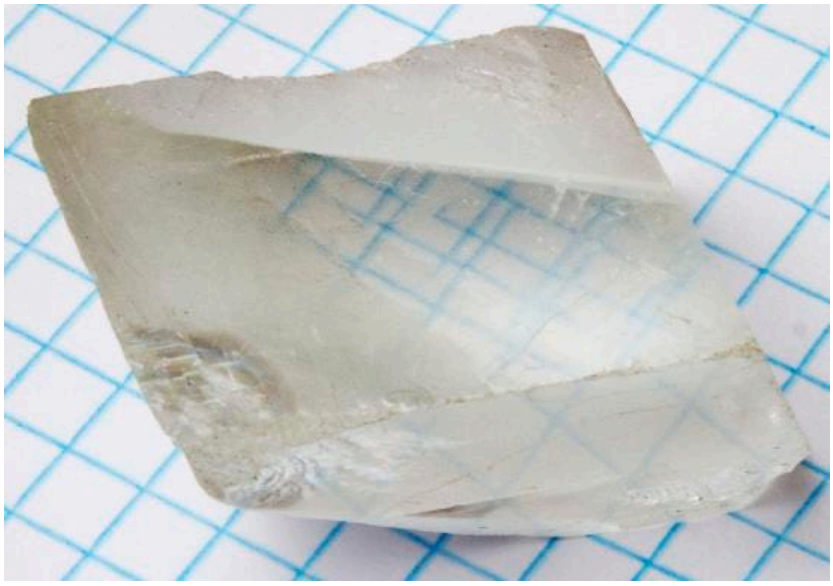
Exercise 18.1.1

One crystalline form of calcium carbonate ($CaCO_3$) is the mineral sold as "calcite" in mineral and gem shops. The solubility of calcite in water is 0.67 mg/100 mL. Calculate its K_{sp}.

Answer available at the end of this section.

The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.

Calcite, a structural material for many organisms, 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. (Cc BY-SA 3.0 Unported; APN MJM via Wikipedia).

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 18.1.1. 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 18.1.2

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. The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 18.1.2) 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.

$$\mathbf{Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)}$$

	$Ca_3(PO_4)_2$	$[Ca^{2+}]$	$[PO_4^{3-}]$
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:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2$$
$$2.07 \times 10^{-33} = 108x^5$$
$$1.92 \times 10^{-35} = x^5$$
$$1.14 \times 10^{-7}\ \text{M} = x$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is $2x$ and $3x$, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

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 18.1.2

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 available at the end of this section.

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 18.1.1, 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.

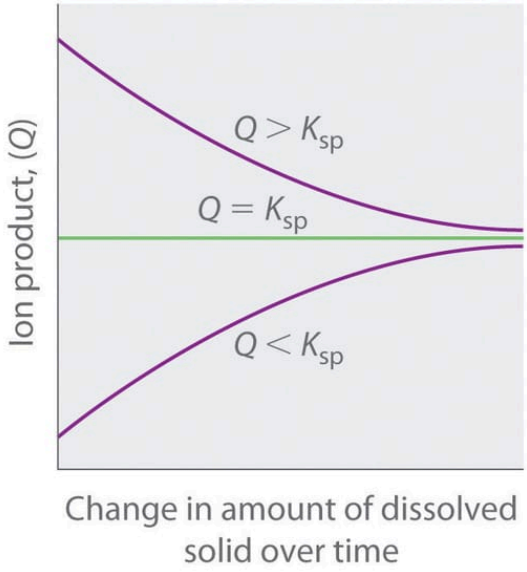


Figure 18.1.1: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, 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.

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 18.1.3

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):

$$\text{moles } Ba^{2+} = 100 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}}\right) = 3.2 \times 10^{-5} \text{ mol } Ba^{2+}$$

$$[Ba^{2+}] = \left(\frac{3.2 \times 10^{-5} \text{ mol } Ba^{2+}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 2.9 \times 10^{-4} \text{ M } Ba^{2+}$$

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):

$$\text{moles } SO_4^{2-} = 10.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.0020 \text{ mol}}{1 \text{ L}}\right) = 2.0 \times 10^{-5} \text{ mol } SO_4^{2-}$$

$$[SO_4^{2-}] = \left(\frac{2.0 \times 10^{-5} \text{ mol } SO_4^{2-}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 1.8 \times 10^{-4} \text{ M } SO_4^{2-}$$

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 18.1.3

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.

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.

Answers

Exercise 18.1.1

4.5×10^{-5}

Exercise 18.1.2

a. 1.28×10^{-4} M
b. 3.54 mg

Exercise 18.1.3

yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)

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18.2: Relationship Between Solubility and Ksp

Learning Objectives

- Quantitatively related K_{sp} to solubility

Considering the relation between solubility and K_{sp} is important when describing the solubility of slightly ionic compounds. However, this article discusses ionic compounds that are difficult to dissolve; they are considered "slightly soluble" or "almost insoluble." Solubility product constants (K_{sq}) are given to those solutes, and these constants can be used to find the molar solubility of the compounds that make the solute. This relationship also facilitates finding the K_{sq} of a slightly soluble solute from its solubility.

Introduction

Recall that the definition of *solubility* is the maximum possible concentration of a solute in a solution at a given temperature and pressure. We can determine the solubility product of a slightly soluble solid from that measure of its solubility at a given temperature and pressure, provided that the only significant reaction that occurs when the solid dissolves is its dissociation into solvated ions, that is, the only equilibrium involved is:

$$\mathrm{M}_p\mathrm{X}_q(s) \rightleftharpoons p\mathrm{M}^{\mathrm{m}+}(aq) + q\mathrm{X}^{\mathrm{n}-}(aq) \tag{18.2.1}$$

In this case, we calculate the solubility product by taking the solid's solubility expressed in units of moles per liter (mol/L), known as its **molar solubility**.

Calculation of K_{sp} from Equilibrium Concentrations

We began the chapter with an informal discussion of how the mineral fluorite is formed. Fluorite, $\mathrm{CaF_2}$, is a slightly soluble solid that dissolves according to the equation:

$$\mathrm{CaF_2}(s) \rightleftharpoons \blacksquare(aq) + 2\,\mathrm{F^-}(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.1×10^{-4} *M*; therefore, that of F^- is 4.2×10^{-4} *M*, that is, twice the concentration of $\mathrm{Ca^{2+}}$. What is the solubility product of fluorite?

Solution

First, write out the K_{sp} expression, then substitute in concentrations and solve for K_{sp}:

$$\mathrm{CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,F^-\,(aq)}$$

A saturated solution is a solution at equilibrium with the solid. Thus:

$$\begin{aligned} K_{\mathrm{sp}} &= [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 \\ &= (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 \\ &= 3.7 \times 10^{-11} \end{aligned}$$

As with other equilibrium constants, we do not include units with K_{sp}.

Exercise 18.2.1

In a saturated solution that is in contact with solid $Mg(OH)_2$, the concentration of Mg^{2+} is 3.7×10^{-5} *M*. What is the solubility product for $Mg(OH)_2$?

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq)$$

Answer available at the end of this section.

Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3×10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The solubility product constant of copper(I) bromide is 6.3×10^{-9}.

The reaction is:

$$\mathrm{CuBr}(s) \rightleftharpoons \mathrm{Cu^+}(aq) + \mathrm{Br^-}(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{sp} = [\mathrm{Cu^+}][\mathrm{Br^-}]$$

Create an ICE table (as introduced in the chapter on fundamental equilibrium concepts), leaving the CuBr column empty as it is a solid and does not contribute to the K_{sp}:

	CuBr ⇌	Cu^+	+ Br^-
Initial concentration (*M*)		0	0
Change (*M*)		*x*	*x*
Equilibrium concentration (*M*)		0 + *x* = *x*	0 + *x* = *x*

At equilibrium:

$$\begin{aligned} K_{sp} &= [\mathrm{Cu^+}][\mathrm{Br^-}] \\ 6.3 \times 10^{-9} &= (x)(x) = x^2 \\ x &= \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5} \end{aligned}$$

Therefore, the molar solubility of CuBr is 7.9×10^{-5} *M*.

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

Finding the Solubility of a Salt: https://youtu.be/98BuldrICXM

Summary

Solubility is defined as the maximum amount of solute that can be dissolved in a solvent at equilibrium. Equilibrium is the state at which the concentrations of products and reactant are constant after the reaction has taken place. The solubility product constant (K_{sp}) describes the equilibrium between a solid and its constituent ions in a solution. The value of the constant identifies the degree to which the compound can dissociate in water. The higher the K_{sp}, the more soluble the compound is. K_{sq} is defined in terms of activity rather than concentration because it is a measure of a concentration that depends on certain conditions such as temperature, pressure, and composition. It is influenced by surroundings. K_{sp} is used to describe the saturated solution of ionic compounds. (A saturated solution is in a state of equilibrium between the dissolved, dissociated, undissolved solid, and the ionic compound.)

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Answers

Exercise 18.2.1

2.0×10^{-13}

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18.3: Common-Ion Effect in Solubility Equilibria

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 hetergeneous 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:

$$[\mathrm{Na}^+] + [\mathrm{K}^+] = [\mathrm{Cl}^-] \tag{18.3.1}$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion. 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.

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.

$$\begin{aligned}
\mathrm{NaCl} &\rightleftharpoons \mathrm{Na}^+ + \mathrm{Cl}^- \\
\mathrm{KCl} &\rightleftharpoons \mathrm{K}^+ + \mathrm{Cl}^- \\
\mathrm{CaCl_2} &\rightleftharpoons \mathrm{Ca}^{2+} + 2\mathrm{Cl}^- \\
\mathrm{AlCl_3} &\rightleftharpoons \mathrm{Al}^{3+} + 3\mathrm{Cl}^- \\
\mathrm{AgCl} &\rightleftharpoons \mathrm{Ag}^+ + \mathrm{Cl}^-
\end{aligned}$$

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 18.3.1

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 18.3.1

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?

$$[\mathrm{Cl}^-] = \frac{0.1\ \mathrm{M} \times 10\ \mathrm{mL} + 0.2\ \mathrm{M} \times 5.0\ \mathrm{mL}}{100.0\ \mathrm{mL}} = 0.020\ \mathrm{M}$$

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 18.3.2

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:

$$\begin{aligned}K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (2s)^2 \\ 1.7 \times 10^{-5} &= 4s^3 \\ s^3 &= \frac{1.7 \times 10^{-5}}{4} \\ &= 4.25 \times 10^{-6} \\ s &= \sqrt[3]{4.25 \times 10^{-6}} \\ &= 1.62 \times 10^{-2}\ mol\ dm^{-3}\end{aligned}$$

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.

A Simple Example

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.

$$[Pb^{2+}] = s \tag{18.3.2}$$

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:

$$[Cl^{-}] = 0.100\ M \tag{18.3.3}$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^{-}]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.00100 \end{aligned} \tag{18.3.4}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3}\ \mathrm{M} \end{aligned} \tag{18.3.5}$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[Pb^{2+}] = 0.0162\ M \tag{18.3.6}$$

Solution in 0.100 M NaCl solution:

$$[Pb^{2+}] = 0.0017\ M \tag{18.3.7}$$

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.

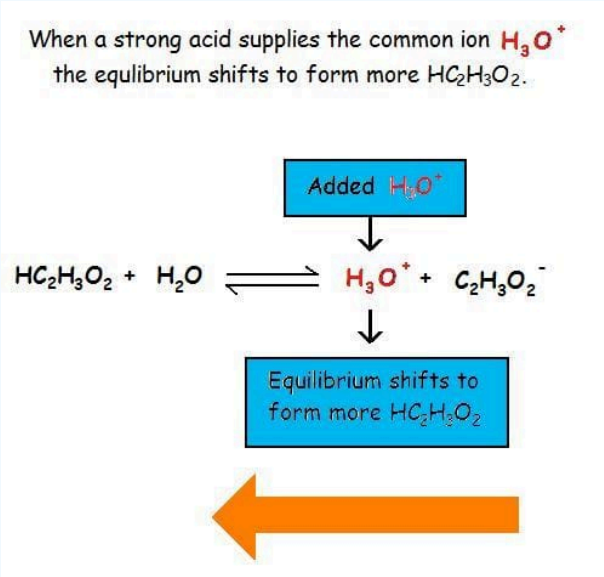
Adding a common ion to a system at equilibrium affects the equilibrium composition, but **not** the ionization constant.

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.

Example 18.3.3

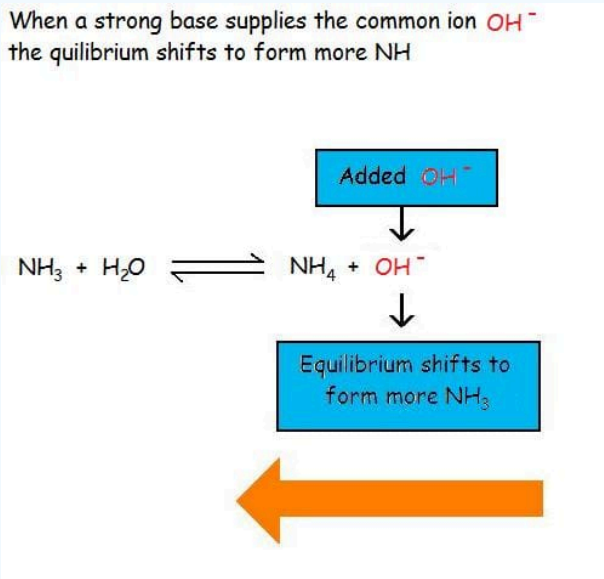
The common ion effect of H_3O^+ on the ionization of acetic acid



The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium.

Example 18.3.4

Consider the common ion effect of OH^- on the ionization of ammonia



Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with Le Châtelier'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.

$$Q_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

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

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$].

$$\mathrm{Ca_3(PO_4)_2\,(s) \rightleftharpoons 3\,Ca^{2+}\,(aq) + 2\,PO_4^{3-}\,(aq)} \tag{18.3.8}$$

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 × 10^{-33}). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains

$$3 \times (1.14 \times 10^{-7}\,M) = 3.42 \times 10^{-7}\,M \tag{18.3.9}$$

and

$$2 \times (1.14 \times 10^{-7}\,M) = 2.28 \times 10^{-7}\,M\,{}_4\mathrm{PO}^{3-} \tag{18.3.10}$$

according to the stoichiometry shown in Equation 18.3.8 (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 18.3.8 to proceed to the left, resulting in precipitation of $\mathrm{Ca_3(PO_4)_2}$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

> 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 18.3.5

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= 1.7×10^{-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.

$$\begin{aligned} Q_{sp} &= [Pb^{2+}][Cl^-]^2 \\ 1.8 \times 10^{-5} &= (s)(2s + 0.1)^2 \end{aligned} \tag{18.3.11}$$

$$\begin{aligned} s &= [Pb^{2+}] \\ &= 1.8 \times 10^{-3} M \\ 2s &= [Cl^-] \\ &\approx 0.1M \end{aligned} \tag{18.3.12}$$

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.

The common ion effect usually decreases the solubility of a sparingly soluble salt.

Example 18.3.6

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 +3*x*, and the change in $[PO_4{}^{3-}]$ is +2*x*. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{18.3.13}$$

	$Ca_3(PO_4)_2$	**$[Ca^{2+}]$**	**$[PO_4{}^{3-}]$**
initial	pure solid	0.20	0
change	—	+3*x*	+2*x*
final	pure solid	0.20 + 3*x*	2*x*

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:

$$K_{sp} = (0.20)^3(2x)^2 = 2.07 \times 10^{-33}$$
$$x^2 = 6.5 \times 10^{-32}$$
$$x = 2.5 \times 10^{-16}\ \text{M}$$

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 18.3.2—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

Exercise 18.3.4

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.

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 Common Ion Effect in Solubility Products: https://youtu.be/_P3wozLs0Tc

Summary

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.

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Answers

Exercise 18.3.4

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)

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18.4: Limitations of the K⍰⍰ Concept

Solubility equilibria defined by a single, simple K_s expression are probably the exception rather than the rule. Such equilibria are often in competition with other reactions with such species as H^+or OH^-, complexing agents, oxidation-reduction, formation of other sparingly soluble species or, in the case of carbonates and sulfites, of gaseous products. The exact treatments of these systems can be extremely complicated, involving the solution of large sets of simultaneous equations. For most practical purposes it is sufficient to recognize the general trends, and to carry out approximate calculations.

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.

The Diverse Ion Effect (The Salt Effect)

A sparingly-soluble salt will be more soluble in a solution that contains non-participating ions. This is just the opposite of the **common ion effect**, and it might at first seem rather counter-intuitive: why would adding more ions of any kind make a salt more likely to dissolve?

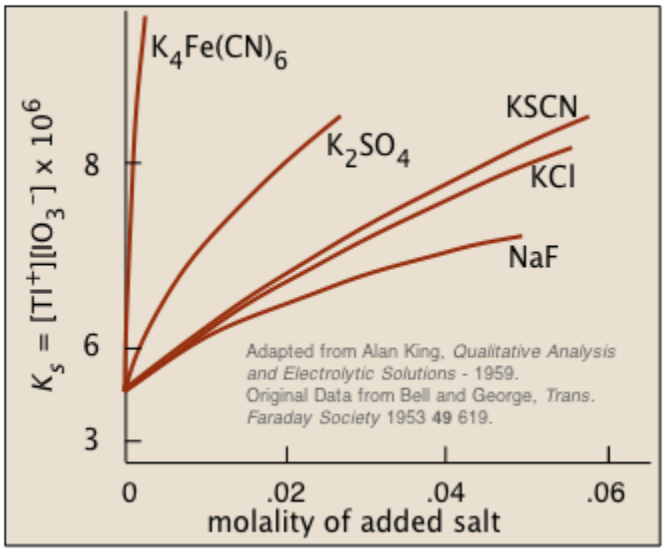


Figure 18.4.1: Solubility of thallium iodate in solutions containing dissolved salts

Although the concentrations of ions in equilibrium with a sparingly soluble solid are so low that they are essentially the same as the activities, the presence of other ions at concentrations of about 0.001 M or greater can materially reduce the activities of the dissolution products, permitting the solubilities to be greater than what simple equilibrium calculations would predict.

> The Diverse Ion Effect typically has the opposite effect on solubility than the common ion effect.

The higher the charge of the foreign ion, the more pronounced is the salt effect. This tells us that inter-ionic (and thus electrostatic) interactions must play a role. The details are rather complicated, but the general idea is that all ions in solution, besides possessing tightly-held waters of hydration, tend to attract oppositely-charged ions ("*counter-ions*") around them. This "atmosphere" of counterions is always rather diffuse, but much less so (and more tightly bound) when one or both kinds of ions have greater charges. From a distance, these ion-counterion pairs (or ion pairs) bodies appear to be almost electrically neutral, which keeps them from interacting with each other (as to form a precipitate).

Example 18.4.1

How does the solubility of $AgCl$ change in absence and presence of $NaNO_3$, given that the molar solubility product of $AgCl$ is 1.76×10^{-10}.

Solution

The Uncommon Ion Effect is a "real" effect and requires the activity definition of K_{sp} to address. The exact definition of the solubility constant is:

$$K_{sp} = a\{Ag^+\} \cdot a\{Cl^-\} = [Ag+]\gamma(Ag^+)[Cl^-]\gamma(Cl^-)$$

Where $a\{Ag^+\}$ and $a\{Cl^-\}$ are the activities of these ions in the presence of the $NaNO_3$. The γ values are the are the corresponding activity coefficients for the ions.

- In dilute solutions (i.e. absence of $NaNO_3$\)

  $$\gamma(Ag^+) = \gamma(Cl^-) = 1$$

  So, the solubility of $AgCl$ is then

  $$[Ag^+] = \sqrt{K_{sp}} = 1.33 \times 10^{-5} \tag{18.4.1}$$

- In the presence of $NaNO_3$, the activity coefficients deviate from unity. So

  $$[Ag^+] = \frac{\sqrt{K_{sp}}}{\sqrt{\gamma(Ag^+)\gamma(Cl^-)}} \tag{18.4.2}$$

  . The denominator has to evaluated from an activity table and is 0.769 so \([Ag^+] = \dfrac{\sqrt{K_{sp}}}{0.769} = 1.73 \times 10^{-5}\].

Hence, in the presence of the $NaNO_3$ soluble salt, the molar solubility of the slightly soluble $AgCl$ salt *increases*. An opposite effect is expected if there were a common ions between the two salts.

Incomplete Dissociation of Solutes into Ions

An **ion pair** consists of a cation and an anion that are in intimate contact in solution, rather than separated by solvent (Figure 18.4.1). 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).

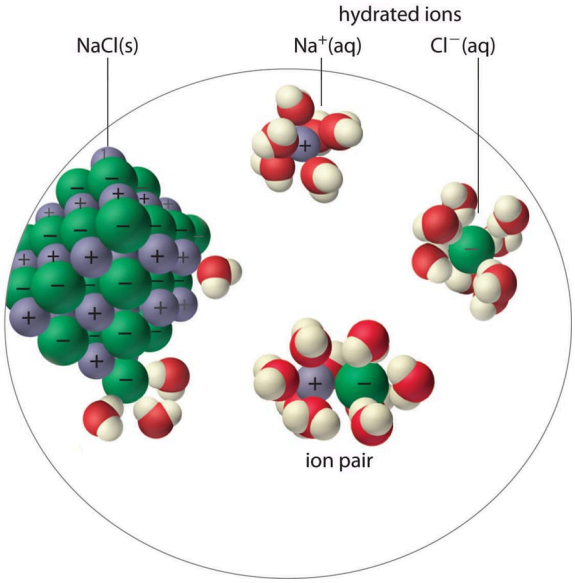


Figure 18.4.2: Ion-Pair Formation. In an ion pair, the cation and the anion are in intimate contact in solution and migrate as a single unit. They are not completely dissociated and individually surrounded by solvent molecules, as are the hydrated ions, which are free to migrate independently.

The overall effect is to reduce the concentrations of the less-shielded ions that are available to combine to form a precipitate. We say that the *thermodynamically-effective concentrations* of these ions are less than their "analytical" concentrations. Chemists refer to these effective concentrations as ionic *activities*, and they denote them by curly brackets $\{Ag^+\}$ as opposed to square brackets $[Ag^+]$ which refer to the nominal or analytical concentrations.

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:

$$\underset{\text{ion pair}}{\mathrm{CaSO_4(s) \rightleftharpoons Ca^{2+} \cdot SO_4^{2-}(aq)}} \rightleftharpoons \mathrm{Ca^{2+}(aq) + SO_4^{2-}(aq)} \tag{18.4.3}$$

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:

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)} \tag{18.4.4}$$

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 $CaSO_4$ 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 $CaSO_4$ to contain a high concentration of ion pairs and its solubility to be greater than predicted from its K_{sp}.

Simultaneous Equilibria (Side Reactions)

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:

$$C_6H_5CO_2H_{(s)} \rightleftharpoons C_6H_5CO_2H_{(aq)} \rightleftharpoons C_6H_5CO^-_{2(aq)} + H^+_{(aq)} \tag{18.4.5}$$

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 18.4.3).

Incomplete dissociation of a molecular solute that is miscible with water can increase the solubility of the solute.

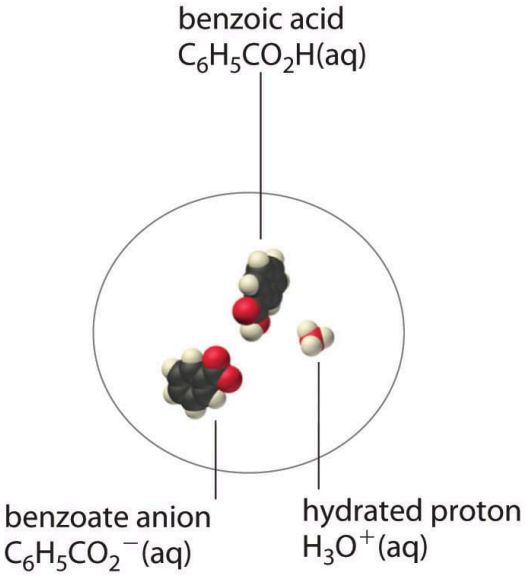


Figure 18.4.3: Incomplete Dissociation of a Molecular Solute. In a saturated solution of benzoic acid in water at 25°C, only about 5% of the dissolved benzoic acid molecules are dissociated to form benzoate anions and hydrated protons. The remaining 95% exists in solution in the form of hydrated neutral molecules. (H_2O molecules are omitted for clarity.)

Although ion pairs, such as $Ca^{2+}•SO_4^{2-}$, 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.

Example 18.4.2: CdI_2 Solubility

The dissolution of cadmium iodide is water is commonly represented as

$$CdI_{2(s)} \rightleftharpoons Cd^{2+} + 2I^- \tag{18.4.6}$$

What you were likely taught about the dissociation of salts in water is wrong! To most students (and to most of their teachers!), this would imply that a 0.1*M* solution of this salt would contain 0.1*M* of Cd^{2+}*(aq)* — and this would be seriously in error because it fails to take into account that the two ions react with each other.

Firstly, they combine to form neutral, largely-covalent molecular species:

$$Cd^{2+}_{(aq)} + 2I^-_{(aq)} \rightarrow CdI_{2(aq)} \tag{18.4.7}$$

This non-ionic form accounts for 78% of the Cd present in the solution! In addition, they form a molecular ion $CdI^-_{(aq)}$ according to the following scheme:

Table 18.4.1: *CdI2 species in solution*

$CdI_{2(s)} \rightleftharpoons Cd^{2+} + 2I^-$	$K_1 = 10^{-3.9}$
$Cd^{2+} + I^- \rightleftharpoons CdI^+$	$K_2 = 10^{+2.3}$
$CdI2_{(s)} \rightleftharpoons CdI^+ + I^-$	$K = 10^{-1.6} = 0.023$

As a consequence, the concentration of "free" Cd^{2+}(aq) in an aqueous cadmium iodide solution is only about 2% of the value you would calculate by taking K_1 as the solubility product. The principal component of such as solution is actually [covalently-bound] CdI_2(aq). It turns out that

Many salts, especially those of metals beyond Group 2, are similarly only partially ionized in aqueous solution:

Table 18.4.2: *Incomplete Dissociation of Select Salts*

salt	molarity	% cation	other species
KCl	0.52	95	KCl(aq) 5%
$MgSO_4$	0.04	58	$MgSO_4$(aq) 42%
$CaCl_2$	0.44	70	$CaCl^+$(aq) 30%
$CuSO_4$	0.045	56	$CuSO_4$(aq) 44%
CdI_2	0.50	2	CdI_2(aq) 76%, CdI^-(aq) 22%
$FeCl_3$	0.1	10	$FeCl^{2+}$(aq) 42%, $FeCl_2$(aq) 40%, $FeOH^{2+}$(aq) 6%, $Fe(OH)_2^+$(aq) 2%

The data shown Tables 18.4.1 and 18.4.2 are taken from the article *Salts are Mostly NOT Ionized* by Stephen Hawkes: 1996 *J Chem Educ.* 73(5) 421-423. This fact was stated by Arrhenius in 1887, but has been largely ignored and is rarely mentioned in standard textbooks.

Summary

The solubility constant, as with all equilibrium constants, are properly defined in terms of *effective concentrations* (activities) and the use of true concentrations to approximate activities in equilibrium constants can often fail. As with all approximations, it is important to understand the conditions that it will fail. three examples are discussed. The salt effect refers to the fact that the presence of a salt which has no ion in common with the solute, has an effect on the ionic strength of the solution and hence on activity coefficients, so that the equilibrium constant, expressed as a concentration quotient, changes.

Contributors and Attributions

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18.5: Criteria for Precipitation and its Completeness

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \blacksquare(aq) + \mathrm{CO_3}^{2-}(aq) \tag{18.5.1}$$

We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient $(\mathrm{Q}=[\mathrm{Ca}^{2+}][\mathrm{CO_3}^{2-}])$ is equal to the solubility product (K_{sp} = 4.8 × 10^{-9}). If we mix a solution of calcium nitrate, which contains Ca^{2+} ions, with a solution of sodium carbonate, which contains $\mathrm{CO_3}^{2-}$ ions, the slightly soluble ionic solid $CaCO_3$ will precipitate, provided that the concentrations of Ca^{2+} and $\mathrm{CO_3}^{2-}$ ions are such that Q is greater than K_{sp} for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of Q equals K_{sp}. A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that Q is less than K_{sp}, then the solution is not saturated and no precipitate will form.

We can compare numerical values of Q with K_{sp} to predict whether precipitation will occur, as Example 18.5.7 shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{sp} = 2.1 \times 10^{-13} \tag{18.5.2}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 *M*?

Solution

This problem asks whether the reaction:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \tag{18.5.3}$$

shifts to the left and forms solid $Mg(OH)_2$ when $[Mg^{2+}]$ = 0.0537 *M* and $[OH^-]$ = 0.0010 *M*. The reaction shifts to the left if Q is greater than K_{sp}. Calculation of the reaction quotient under these conditions is shown here:

$$\mathrm{Q} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8} \tag{18.5.4}$$

Because Q is greater than K_{sp} (Q = 5.4 × 10^{-8} is larger than K_{sp} = 2.1 × 10^{-13}), we can expect the reaction to shift to the left and form solid magnesium hydroxide. $Mg(OH)_2(s)$ forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of Q is equal to K_{sp}.

Exercise 18.5.1

Use the solubility products in Appendix J to determine whether $CaHPO_4$ will precipitate from a solution with $[Ca^{2+}]$ = 0.0001 *M* and $[\mathrm{HPO_4}^{2-}]$ = 0.001 *M*.

Answer

No precipitation of $CaHPO_4$; Q = 1 × 10^{-7}, which is less than K_{sp}

Precipitation of AgCl upon Mixing Solutions

Does silver chloride precipitate when equal volumes of a 2.0 × 10^{-4}-*M* solution of $AgNO_3$ and a 2.0 × 10^{-4}-*M* solution of NaCl are mixed?

(Note: The solution also contains Na^+ and NO_3^- ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The solubility product is 1.8 × 10^{-10} (see Appendix J).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. The volume doubles when we mix equal volumes of $AgNO_3$ and NaCl solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing, [Ag^+] and [Cl^-] are both equal to:

$$\frac{1}{2}(2.0 \times 10^{-4})\ M = 1.0 \times 10^{-4}\ M$$

The reaction quotient, Q, is *momentarily* greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [Ag^+][Cl^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sp}$$

Since supersaturated solutions are unstable, AgCl will precipitate from the mixture until the solution returns to equilibrium, with Q equal to K_{sp}.

Exercise 18.5.2

Will $KClO_4$ precipitate when 20 mL of a 0.050-*M* solution of K^+ is added to 80 mL of a 0.50-*M* solution of ClO_4^-? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

Answer

No, Q = 4.0 × 10^{-3}, which is less than K_{sp} = 1.07 × 10^{-2}

In the previous two examples, we have seen that $Mg(OH)_2$ or AgCl precipitate when Q is greater than K_{sp}. In general, when a solution of a soluble salt of the M^{m+} ion is mixed with a solution of a soluble salt of the X^{n-} ion, the solid, M_pX_q precipitates if the value of Q for the mixture of M^{m+} and X^{n-} is greater than K_{sp} for M_pX_q. Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $C_2O_4^{2-}$, for this purpose (Figure 18.5.4). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4 \cdot H_2O$ (which also contains water bound in the solid). The concentration of Ca^{2+} in a sample of blood serum is 2.2 × 10^{-3} *M*. What concentration of $C_2O_4^{2-}$ ion must be established before $CaC_2O_4 \cdot H_2O$ begins to precipitate?



Figure 18.5.4: Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:

$$CaC_2O_4(s) \rightleftharpoons [redacted](aq) + {C_2O_4}^{2-}(aq) \tag{18.5.5}$$

For this reaction:

$$K_{sp} = [Ca^{2+}][{C_2O_4}^{2-}] = 2.27 \times 10^{-9} \tag{18.5.6}$$

(see Appendix J)

CaC_2O_4 does not appear in this expression because it is a solid. Water does not appear because it is the solvent.

Solid CaC_2O_4 does not begin to form until Q equals K_{sp}. Because we know K_{sp} and $[Ca^{2+}]$, we can solve for the concentration of ${C_2O_4}^{2-}$ that is necessary to produce the first trace of solid:

$$\begin{gathered} Q = K_{sp} = [Ca^{2+}][{C_2O_4}^{2-}] = 2.27 \times 10^{-9} \\ (2.2 \times 10^{-3})[{C_2O_4}^{2-}] = 2.27 \times 10^{-9} \\ [{C_2O_4}^{2-}] = \frac{2.27 \times 10^{-9}}{2.2 \times 10^{-3}} = 1.0 \times 10^{-6} \end{gathered}$$

A concentration of $[{C_2O_4}^{2-}] = 1.0 \times 10^{-6}$ *M* is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Exercise 18.5.3

If a solution contains 0.0020 mol of ${CrO_4}^{2-}$ per liter, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer:

7.0×10^{-5} *M*

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of K_{sp} and the concentration of one ion in solution, we can calculate the

concentration of the second ion remaining in solution. The calculation is of the same type as that in Example—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

Concentrations Following Precipitation

Clothing washed in water that has a manganese [$Mn^{2+}(aq)$] concentration exceeding 0.1 mg/L (1.8×10^{-6} *M*) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide, $Mn(OH)_2$, what pH is required to keep [Mn^{2+}] equal to 1.8×10^{-6} *M*?

Solution The dissolution of $Mn(OH)_2$ is described by the equation:

$$\mathrm{Mn(OH)_2}(s) \rightleftharpoons \mathrm{Mn^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{\mathrm{sp}} = 4.5 \times 10^{-14} \tag{18.5.7}$$

We need to calculate the concentration of OH^- when the concentration of Mn^{2+} is 1.8×10^{-6} *M*. From that, we calculate the pH. At equilibrium:

$$K_{\mathrm{sp}} = [\mathrm{Mn^{2+}}][\mathrm{OH^-}]^2 \tag{18.5.8}$$

or

$$(1.8 \times 10^{-6})[\mathrm{OH^-}]^2 = 4.5 \times 10^{-14} \tag{18.5.9}$$

so

$$[\mathrm{OH^-}] = 1.6 \times 10^{-4}\ M \tag{18.5.10}$$

Now we calculate the pH from the pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.6 \times 10^{-4}) = 3.80$$
$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 3.80 = 10.20$$

If the person doing laundry adds a base, such as the sodium silicate (Na_4SiO_4) in some detergents, to the wash water until the pH is raised to 10.20, the manganese ion will be reduced to a concentration of 1.8×10^{-6} *M*; at that concentration or less, the ion will not stain clothing.

Exercise 18.5.4

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} *M*. Calculate the pH at which [Mg^{2+}] is diminished to 1.0×10^{-5} *M* by the addition of $Ca(OH)_2$.

Answer

11.09

Due to their light sensitivity, mixtures of silver halides are used in fiber optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though AgCl ($K_{sp} = 1.6 \times 10^{-10}$), AgBr ($K_{sp} = 7.7 \times 10^{-13}$), and AgI ($K_{sp} = 8.3 \times 10^{-17}$) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding Ag^+ to a solution of Cl^-, Br^-, and I^-; essentially all of the AgI will precipitate before any of the other solid halides form because of its smaller value for K_{sp}. However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of Cl^-, Br^-, and I^- to a solution of Ag^+.

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller K_{sp}) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the K_{sp} values of the two compounds differ by two orders of magnitude or more (e.g., 10^{-2} vs. 10^{-4}), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of selective precipitation, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.

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Determining if a Precipitate forms (The Ion Product): https://youtu.be/Naf7PoHPz8Y

Summary

A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product. A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution. The common ion effect can also play a role in precipitation reactions. In the presence of an ion in common with one of the ions in the solution, Le Chatelier's principle applies and more precipitate comes out of solution so that the molar solubility is reduced.

Glossary

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

molar solubility
: solubility of a compound expressed in units of moles per liter (mol/L)

selective precipitation
: process in which ions are separated using differences in their solubility with a given precipitating reagent

solubility product (K_{sp})
: equilibrium constant for the dissolution of a slightly soluble electrolyte

Contributors and Attributions

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18.6: Fractional Precipitation

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 18.6.1

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 18.6.2

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 18.6.1, $[\mathrm{CrO_4{}^{2-}}] = 3.6 \times 10^{-4}\ M$ 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 18.6.3

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^+?

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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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18.7: Solubility and pH

Learning Objectives

- To understand why the solubility of many compounds depends on pH.

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. In this section, we discuss the relationship between the solubility of these classes of compounds and pH.

The Effect of Acid–Base Equilibria the Solubility of Salts

We begin our discussion by examining the effect of pH on the solubility of a representative salt, $\mathrm{M^+A^-}$, where $\mathrm{A^-}$ is the conjugate base of the weak acid HA. When the salt dissolves in water, the following reaction occurs:

$$\mathrm{MA\,(s)} \rightleftharpoons \mathrm{M^+\,(aq) + A^-\,(aq)}$$

with

$$K_{sp} = [\mathrm{M^+}][\mathrm{A^-}]$$

The anion can also react with water in a hydrolysis reaction:

$$\mathrm{A^-\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{OH^-\,(aq) + HA\,(aq)} \tag{18.7.1}$$

Because of the reaction described in Equation 18.7.1, the predicted solubility of a sparingly soluble salt that has a basic anion such as S^{2-}, PO_4^{3-}, or CO_3^{2-} is increased. If instead a strong acid is added to the solution, the added H^+ will react essentially completely with A^- to form HA. This reaction decreases $[A^-]$, which decreases the magnitude of the ion product

$$Q = [\mathrm{M^+}][\mathrm{A^-}] \tag{18.7.2}$$

According to Le Chatelier's principle, more MA will dissolve until $Q = K_{sp}$. Hence an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid. In contrast, pH has little to no effect on the solubility of salts whose anion is the conjugate base of a stronger weak acid or a strong acid, respectively (e.g., chlorides, bromides, iodides, and sulfates). For example, the hydroxide salt $Mg(OH)_2$ is relatively insoluble in water:

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \tag{18.7.3}$$

with

$$K_{sp} = 5.61 \times 10^{-12} \tag{18.7.4}$$

When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing OH^- from solution:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \tag{18.7.5}$$

The overall equation for the reaction of $Mg(OH)_2$ with acid is thus

$$Mg(OH)_{2(s)} + 2H^+(aq) \rightleftharpoons Mg^{2+}(aq) + 2H_2O(l) \tag{18.7.6}$$

As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in Equation 18.7.6 is driven to the right, so more $Mg(OH)_2$ dissolves.

Such pH-dependent solubility is not restricted to salts that contain anions derived from water. For example, CaF_2 is a sparingly soluble salt:

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}(aq) + 2F^{-}(aq) \tag{18.7.7}$$

with

$$K_{sp} = 3.45 \times 10^{-11} \tag{18.7.8}$$

When strong acid is added to a saturated solution of CaF_2, the following reaction occurs:

$$H^{+}(aq) + F^{-}(aq) \rightleftharpoons HF(aq) \tag{18.7.9}$$

Because the forward reaction decreases the fluoride ion concentration, more CaF_2 dissolves to relieve the stress on the system. The net reaction of CaF_2 with strong acid is thus

$$CaF_{2(s)} + 2H^{+}(aq) \rightarrow Ca^{2+}(aq) + 2HF(aq) \tag{18.7.10}$$

Example 18.7.1 shows how to calculate the solubility effect of adding a strong acid to a solution of a sparingly soluble salt.

Sparingly soluble salts derived from weak acids tend to be more soluble in an acidic solution.

Example 18.7.1

Lead oxalate (PbC_2O_4), lead iodide (PbI_2), and lead sulfate ($PbSO_4$) are all rather insoluble, with K_{sp} values of 4.8×10^{-10}, 9.8×10^{-9}, and 2.53×10^{-8}, respectively. What effect does adding a strong acid, such as perchloric acid, have on their relative solubilities?

Given: K_{sp} values for three compounds

Asked for: relative solubilities in acid solution

Strategy:

Write the balanced chemical equation for the dissolution of each salt. Because the strongest conjugate base will be most affected by the addition of strong acid, determine the relative solubilities from the relative basicity of the anions.

Solution

The solubility Equilibria for the three salts are as follows:

$$PbC_2O_{4(s)} \rightleftharpoons Pb^{2+}(aq) + C_2O^{2-}_{4(aq)}$$

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}(aq) + 2I^{-}(aq)$$

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}(aq) + SO^{2-}_{4(aq)}$$

The addition of a strong acid will have the greatest effect on the solubility of a salt that contains the conjugate base of a weak acid as the anion. Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of PbI_2 will not greatly affect its solubility; the acid will simply dissociate to form H^+(aq) and the corresponding anion. In contrast, oxalate is the fully deprotonated form of oxalic acid (HO_2CCO_2H), which is a weak diprotic acid ($pK_{a1} = 1.23$ and $pK_{a2} = 4.19$). Consequently, the oxalate ion has a significant affinity for one proton and a lower affinity for a second proton. Adding a strong acid to a saturated solution of lead oxalate will result in the following reactions:

$$C_2O^{2-}_{4(aq)} + H^{+}(aq) \rightarrow HO_2CCO^{-}_{2(aq)}$$

$$HO_2CCO^{-}_{2(aq)} + H^{+}(aq) \rightarrow HO_2CCO_2H(aq)$$

These reactions will decrease [$C_2O_4^{2-}$], causing more lead oxalate to dissolve to relieve the stress on the system. The pK_a of HSO_4^- (1.99) is similar in magnitude to the pK_{a1} of oxalic acid, so adding a strong acid to a saturated solution of $PbSO_4$ will result in the following reaction:

$$SO^{2-}_{4(aq)} + H^+(aq) \rightleftharpoons HSO^-_{4(aq)}$$

Because HSO_4^- has a pKa of 1.99, this reaction will lie largely to the left as written. Consequently, we predict that the effect of added strong acid on the solubility of $PbSO_4$ will be significantly less than for PbC_2O_4.

Exercise 18.7.1

Which of the following insoluble salts—AgCl, Ag_2CO_3, Ag_3PO_4, and/or AgBr—will be substantially more soluble in 1.0 M HNO_3 than in pure water?

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

Solubility Products and pH: https://youtu.be/XJ0s5SATZgQ

Caves and their associated pinnacles and spires of stone provide one of the most impressive examples of pH-dependent solubility Equilbria(part (a) in Figure 18.7.1:). Perhaps the most familiar caves are formed from limestone, such as Carlsbad Caverns in New Mexico, Mammoth Cave in Kentucky, and Luray Caverns in Virginia. The primary reactions that are responsible for the formation of limestone caves are as follows:

$$\mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)} \tag{18.7.11}$$

$$\mathrm{HCO_3^-\,(aq) \rightleftharpoons H^+\,(aq) + CO_3^{2-}\,(aq)} \tag{18.7.12}$$

$$\mathrm{Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightleftharpoons CaCO_3\,(s)} \tag{18.7.13}$$

Limestone deposits that form caves consist primarily of $CaCO_3$ from the remains of living creatures such as clams and corals, which used it for making structures such as shells. When a saturated solution of $CaCO_3$ in CO_2-rich water rises toward Earth's surface or is otherwise heated, CO_2 gas is released as the water warms. $CaCO_3$ then precipitates from the solution according to the following equation (part (b) in Figure 18.7.1:):

$$Ca^{2+}(aq) + 2HCO^-_{3(aq)} \rightleftharpoons CaCO_{3(s)} + CO_{2(g)} + H_2O(l) \tag{18.7.14}$$

The forward direction is the same reaction that produces the solid called scale in teapots, coffee makers, water heaters, boilers, and other places where hard water is repeatedly heated.



Figure 18.7.1: The Chemistry of Cave Formation. (a) This cave in Campanet, Mallorca, Spain, and its associated formations are examples of pH-dependent solubility equilibriums. (b) A cave forms when groundwater containing atmospheric CO_2, forming an acidic solution, dissolves limestone ($CaCO_3$) in a process that may take tens of thousands of years. As groundwater seeps into a cave, water evaporates from the solution of $CaCO_3$ in CO_2-rich water, producing a supersaturated solution and a shift in equilibrium that causes precipitation of the $CaCO_3$. The deposited limestone eventually forms stalactites and stalagmites.

When groundwater-containing atmospheric CO_2 (Equations 18.7.11 and 18.7.12) finds its way into microscopic cracks in the limestone deposits, $CaCO_3$ dissolves in the acidic solution in the reverse direction of Equation 18.7.14. The cracks gradually enlarge from 10–50 μm to 5–10 mm, a process that can take as long as 10,000 yr. Eventually, after about another 10,000 yr, a cave forms. Groundwater from the surface seeps into the cave and clings to the ceiling, where the water evaporates and causes the equilibrium in Equation 18.7.14 to shift to the right. A circular layer of solid $CaCO_3$ is deposited, which eventually produces a long, hollow spire of limestone called a stalactite that grows down from the ceiling. Below, where the droplets land when they fall from the ceiling, a similar process causes another spire, called a stalagmite, to grow up. The same processes that carve out hollows below ground are also at work above ground, in some cases producing fantastically convoluted landscapes like that of Yunnan Province in China (Figure 18.7.2).

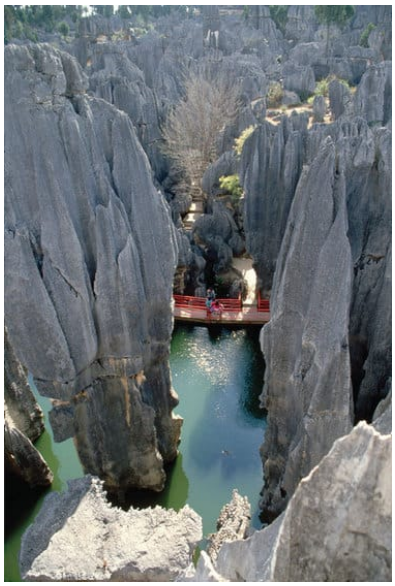


Figure 18.7.2: Solubility Equilbriain the Formation of Karst Landscapes. Landscapes such as the steep limestone pinnacles of the Stone Forest in Yunnan Province, China, are formed from the same process that produces caves and their associated formations.

Acidic, Basic, and Amphoteric Oxides and Hydroxides

One of the earliest classifications of substances was based on their solubility in acidic versus basic solution, which led to the classification of oxides and hydroxides as being either basic or acidic. **Basic oxides** and hydroxides either react with water to produce a basic solution or dissolve readily in aqueous acid. **Acidic oxides** or hydroxides either react with water to produce an acidic solution or are soluble in aqueous base. There is a clear correlation between the acidic or the basic character of an oxide and the position of the element combined with oxygen in the periodic table. Oxides of metallic elements are generally basic oxides, and oxides of nonmetallic elements are acidic oxides. Compare, for example, the reactions of a typical metal oxide, cesium oxide, and a typical nonmetal oxide, sulfur trioxide, with water:

$$Cs_2O(s) + H_2O(l) \rightarrow 2Cs^+(aq) + 2OH^-(aq) \tag{18.7.15}$$

$$SO_{3(g)} + H_2O(l) \rightarrow H_2SO_{4(aq)} \tag{18.7.16}$$

Cesium oxide reacts with water to produce a basic solution of cesium hydroxide, whereas sulfur trioxide reacts with water to produce a solution of sulfuric acid—very different behaviors indeed

Metal oxides generally react with water to produce basic solutions, whereas nonmetal oxides produce acidic solutions.

The difference in reactivity is due to the difference in bonding in the two kinds of oxides. Because of the low electronegativity of the metals at the far left in the periodic table, their oxides are best viewed as containing discrete M^{n+} cations and O^{2-} anions. At the other end of the spectrum are nonmetal oxides; due to their higher electronegativities, nonmetals form oxides with covalent bonds to oxygen. Because of the high electronegativity of oxygen, however, the covalent bond between oxygen and the other atom, E, is usually polarized: $E^{\delta+}$–$O^{\delta-}$. The atom E in these oxides acts as a Lewis acid that reacts with the oxygen atom of water to produce an oxoacid. Oxides of metals in high oxidation states also tend to be acidic oxides for the same reason: they contain covalent bonds to oxygen. An example of an acidic metal oxide is MoO_3, which is insoluble in both water and acid but dissolves in strong base to give solutions of the molybdate ion (MoO_4^{2-}):

$$MoO_{3(s)} + 2OH^-(aq) \rightarrow MoO^{2-}_{4(aq)} + H_2O(l) \tag{18.7.17}$$

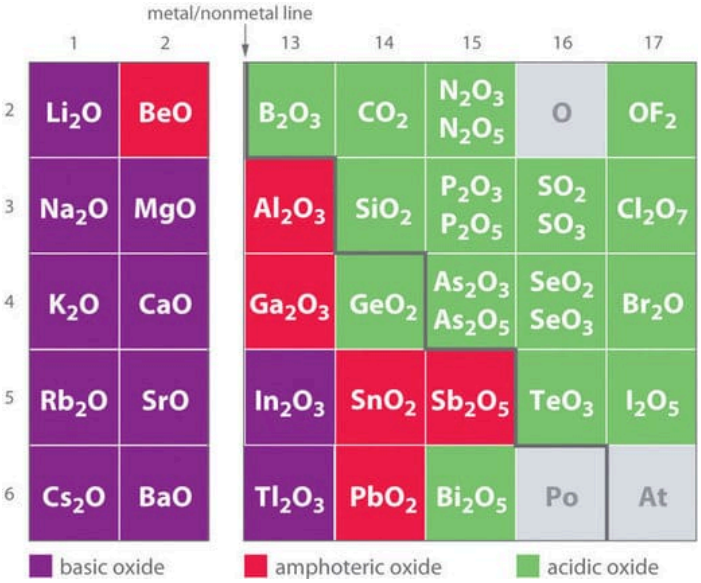


Figure 18.7.3: Classification of the Oxides of the Main Group Elements According to Their Acidic or Basic Character. There is a gradual transition from basic oxides to acidic oxides from the lower left to the upper right in the periodic table. Oxides of metallic elements are generally basic oxides, which either react with water to form a basic solution or dissolve in aqueous acid. In contrast, oxides of nonmetallic elements are acidic oxides, which either react with water to form an acidic solution or are soluble in aqueous base. Oxides of intermediate character, called amphoteric oxides, are located along a diagonal line between the two extremes. Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex ion. (Radioactive elements are not classified.)

As shown in Figure 18.7.3, there is a gradual transition from basic metal oxides to acidic nonmetal oxides as we go from the lower left to the upper right in the periodic table, with a broad diagonal band of oxides of intermediate character separating the

two extremes. Many of the oxides of the elements in this diagonal region of the periodic table are soluble in both acidic and basic solutions; consequently, they are called **amphoteric oxides** (from the Greek ampho, meaning "both," as in amphiprotic). Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex. As shown in Video 18.7.1, for example, mixing the amphoteric oxide $Cr(OH)_3$ (also written as $Cr_2O_3•3H_2O$) with water gives a muddy, purple-brown suspension. Adding acid causes the $Cr(OH)_3$ to dissolve to give a bright violet solution of $Cr^{3+}(aq)$, which contains the $[Cr(H_2O)_6]^{3+}$ ion, whereas adding strong base gives a green solution of the $[Cr(OH)_4]^-$ ion. The chemical equations for the reactions are as follows:

$$\underset{\text{violet}}{Cr^{3+}(aq)} + 3H_2O(l) \leftarrow Cr(OH)_3(s) + 3H^+(aq) \tag{18.7.18}$$

$$\underset{\text{green}}{[Cr(OH)_4]^-(aq)} \leftarrow Cr(OH)_3(s) + OH^-(aq) \tag{18.7.19}$$

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 18.7.1***:*** *Chromium(III) Hydroxide [$Cr(OH)_3$ or $Cr_2O_3•3H_2O$] is an Example of an Amphoteric Oxide. All three beakers originally contained a suspension of brownish purple $Cr(OH)_3$(s) (center). When concentrated acid (6 M H_2SO_4) was added to the beaker on the left, $Cr(OH)_3$ dissolved to produce violet $[Cr(H_2O)_6]^{3+}$ ions and water. The addition of concentrated base (6 M NaOH) to the beaker on the right caused $Cr(OH)_3$ to dissolve, producing green $[Cr(OH)_4]^-$ ions. For a more complete description, see https://www.youtube.com/watch?v=IQNcLH6OZK0*

Example 18.7.2

Aluminum hydroxide, written as either $Al(OH)_3$ or $Al_2O_3•3H_2O$, is amphoteric. Write chemical equations to describe the dissolution of aluminum hydroxide in (a) acid and (b) base.

Given: amphoteric compound

Asked for: dissolution reactions in acid and base

Strategy:

Using Equations 18.7.18 and 18.7.19 as a guide, write the dissolution reactions in acid and base solutions.

Solution

a. An acid donates protons to hydroxide to give water and the hydrated metal ion, so aluminum hydroxide, which contains three OH^- ions per Al, needs three H^+ ions:

$$Al(OH)_{3(s)} + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$$

In aqueous solution, Al^{3+} forms the complex ion $[Al(H_2O)_6]^{3+}$.

b. In basic solution, OH^- is added to the compound to produce a soluble and stable poly(hydroxo) complex:

$$Al(OH)_{3(s)} + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$$

Exercise 18.7.2

Copper(II) hydroxide, written as either $Cu(OH)_2$ or $CuO•H_2O$, is *amphoteric*. Write chemical equations that describe the dissolution of cupric hydroxide both in an acid and in a base.

Answer available at the end of this section.

Selective Precipitation Using pH

Many dissolved metal ions can be separated by the selective precipitation of the cations from solution under specific conditions. In this technique, pH is often used to control the concentration of the anion in solution, which controls which cations precipitate.

> The concentration of anions in solution can often be controlled by adjusting the pH, thereby allowing the selective precipitation of cations.

Suppose, for example, we have a solution that contains 1.0 mM Zn^{2+} and 1.0 mM Cd^{2+} and want to separate the two metals by selective precipitation as the insoluble sulfide salts, ZnS and CdS. The relevant solubility equilbria can be written as follows:

$$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq) \tag{18.7.20}$$

with

$$K_{sp} = 1.6 \times 10^{-24} \tag{18.7.21}$$

and

$$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq) \tag{18.7.22}$$

with

$$K_{sp} = 8.0 \times 10^{-27} \tag{18.7.23}$$

Because the S^{2-} ion is quite basic and reacts extensively with water to give HS^- and OH^-, the solubility equilbria are more accurately written as $MS(s) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-$ rather than $MS(s) \rightleftharpoons M^{2+}(aq) + S^{2-}(aq)$. Here we use the simpler form involving S^{2-}, which is justified because we take the reaction of S^{2-} with water into account later in the solution, arriving at the same answer using either equilibrium equation.

The sulfide concentrations needed to cause ZnS and CdS to precipitate are as follows:

$$K_{sp} = [Zn^{2+}][S^{2-}] \tag{18.7.24}$$

$$1.6 \times 10^{-24} = (0.0010\ M)[S^{2-}] \tag{18.7.25}$$

$$1.6 \times 10^{-21}\ M = [S^{2-}] \tag{18.7.26}$$

and

$$K_{sp} = [Cd^{2+}][S^{2-}] \tag{18.7.27}$$

$$8.0 \times 10^{-27} = (0.0010\ M)[S^{2-}] \tag{18.7.28}$$

$$8.0 \times 10^{-24}\ M = [S^{2-}] \tag{18.7.29}$$

Thus sulfide concentrations between 1.6×10^{-21} M and 8.0×10^{-24} M will precipitate CdS from solution but not ZnS. How do we obtain such low concentrations of sulfide? A saturated aqueous solution of H_2S contains 0.10 M H_2S at 20°C. The pK_{a1} for H_2S is 6.97, and pK_{a2} corresponding to the formation of $[S^{2-}]$ is 12.90. The equations for these reactions are as follows:

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \tag{18.7.30}$$

with

$$pK_{a1} = 6.97 \text{ and hence } K_{a1} = 1.1 \times 10^{-7} \tag{18.7.31}$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq) \tag{18.7.32}$$

with

$$pK_{a2} = 12.90 \text{ and hence } K_{a2} = 1.3 \times 10^{-13} \tag{18.7.33}$$

We can show that the concentration of S^{2-} is 1.3×10^{-13} by comparing K_{a1} and K_{a2} and recognizing that the contribution to $[H^+]$ from the dissociation of HS^- is negligible compared with $[H^+]$ from the dissociation of H_2S. Thus substituting 0.10 M in the equation for K_{a1} for the concentration of H_2S, which is essentially constant regardless of the pH, gives the following:

$$K_{a1} = 1.1 \times 10^{-7} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{x^2}{0.10 \text{ M}} \tag{18.7.34}$$

$$x = 1.1 \times 10^{-4} \text{ M} = [H^+] = [HS^-]$$

Substituting this value for $[H^+]$ and $[HS^-]$ into the equation for K_{a2},

$$K_{a2} = 1.3 \times 10^{-13} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(1.1 \times 10^{-4} \text{ M})x}{1.1 \times 10^{-4} \text{ M}} = x = [S^{2-}] \tag{18.7.35}$$

Although $[S^{2-}]$ in an H_2S solution is very low (1.3×10^{-13} M), bubbling H_2S through the solution until it is saturated would precipitate both metal ions because the concentration of S^{2-} would then be much greater than 1.6×10^{-21} M. Thus we must adjust $[S^{2-}]$ to stay within the desired range. The most direct way to do this is to adjust $[H^+]$ by adding acid to the H_2S solution (recall Le Chatelier's principle), thereby driving the equilibrium in Equation 18.7.33 to the left. The overall equation for the dissociation of H_2S is as follows:

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq) \tag{18.7.36}$$

Now we can use the equilibrium constant K for the overall reaction, which is the product of K_{a1} and K_{a2}, and the concentration of H_2S in a saturated solution to calculate the H^+ concentration needed to produce $[S^{2-}]$ of 1.6×10^{-21} M:

$$K = K_{a1}K_{a2} = (1.1 \times 10^{-7})(1.3 \times 10^{-13}) = 1.4 \times 10^{-20} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \tag{18.7.37}$$

$$[H^+]^2 = \frac{K[H_2S]}{[S^{2-}]} = \frac{(1.4 \times 10^{-20})(0.10 \text{ M})}{1.6 \times 10^{-21} \text{ M}} = 0.88 \tag{18.7.38}$$

$$[H^+] = 0.94 \tag{18.7.39}$$

Thus adding a strong acid such as HCl to make the solution 0.94 M in H^+ will prevent the more soluble ZnS from precipitating while ensuring that the less soluble CdS will precipitate when the solution is saturated with H_2S.

Example 18.7.3

A solution contains 0.010 M Ca^{2+} and 0.010 M La^{3+}. What concentration of HCl is needed to precipitate $La_2(C_2O_4)_3 \cdot 9H_2O$ but not $Ca(C_2O_4) \cdot H_2O$ if the concentration of oxalic acid is 1.0 M? K_{sp} values are 2.32×10^{-9} for $Ca(C_2O_4)$ and 2.5×10^{-27} for $La_2(C_2O_4)_3$; $pK_{a1} = 1.25$ and $pK_{a2} = 3.81$ for oxalic acid.

Given: concentrations of cations, K_{sp} values, and concentration and pK_a values for oxalic acid

Asked for: concentration of HCl needed for selective precipitation of $La_2(C_2O_4)_3$

Strategy:

A. Write each solubility product expression and calculate the oxalate concentration needed for precipitation to occur. Determine the concentration range needed for selective precipitation of $La_2(C_2O_4)_3•9H_2O$.
B. Add the equations for the first and second dissociations of oxalic acid to get an overall equation for the dissociation of oxalic acid to oxalate. Substitute the [ox^{2-}] needed to precipitate $La_2(C_2O_4)_3•9H_2O$ into the overall equation for the dissociation of oxalic acid to calculate the required [H^+].

Solution

A Because the salts have different stoichiometries, we cannot directly compare the magnitudes of the solubility products. Instead, we must use the equilibrium constant expression for each solubility product to calculate the concentration of oxalate needed for precipitation to occur. Using ox^{2-} for oxalate, we write the solubility product expression for calcium oxalate as follows:

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (0.010)[ox^{2-}] = 2.32 \times 10^{-9}$$

$$[ox^{2-}] = 2.32 \times 10^{-7}\ M$$

The expression for lanthanum oxalate is as follows:

$$K_{sp} = [La^{3+}]^2[ox^{2-}]^3 = (0.010)^2[ox^{2-}]^3 = 2.5 \times 10^{-27}$$

$$[ox^{2-}] = 2.9 \times 10^{-8}\ M$$

Thus lanthanum oxalate is less soluble and will selectively precipitate when the oxalate concentration is between $2.9 \times 10^{-8} M$ and $2.32 \times 10^{-7} M$.

B To prevent Ca^{2+} from precipitating as calcium oxalate, we must add enough H^+ to give a maximum oxalate concentration of 2.32×10^{-7} M. We can calculate the required [H^+] by using the overall equation for the dissociation of oxalic acid to oxalate:

$$HO_2CCO_2H(aq) \rightleftharpoons 2H^+(aq) + C_2O_{4(aq)}^{2-} \tag{18.7.40}$$

$$K = K_{a1}K_{a2} = (10^{-1.25})(10^{-3.81}) = 10^{-5.06} = 8.7 \times 10^{-6}$$

Substituting the desired oxalate concentration into the equilibrium constant expression,

$$8.7 \times 10^{-6} = \frac{[\mathrm{H^+}]^2[\mathrm{ox^{2-}}]}{[\mathrm{HO_2CCO_2H}]} = \frac{[\mathrm{H^+}]^2(2.32 \times 10^{-7})}{1.0} \tag{18.7.41}$$

$$[\mathrm{H^+}] = 6.1\ \mathrm{M} \tag{18.7.42}$$

Thus adding enough HCl to give [H^+] = 6.1 M will cause only $La_2(C_2O_4)_3•9H_2O$ to precipitate from the solution.

Exercise 18.7.3

A solution contains 0.015 M Fe^{2+} and 0.015 M Pb^{2+}. What concentration of acid is needed to ensure that Pb^{2+} precipitates as PbS in a saturated solution of H_2S, but Fe^{2+} does not precipitate as FeS? K_{sp} values are 6.3×10^{-18} for FeS and 8.0×10^{-28} for PbS.

Answer available at the end of this section.

Summary

The anion in sparingly soluble salts is often the conjugate base of a weak acid that may become protonated in solution,

so the solubility of simple oxides and sulfides, both strong bases, often depends on pH. The anion in many sparingly soluble salts is the conjugate base of a weak acid. At low pH, protonation of the anion can dramatically increase the solubility of the salt. Oxides can be classified as acidic oxides or basic oxides. Acidic oxides either react with water to give an acidic solution or dissolve in strong base; most acidic oxides are nonmetal oxides or oxides of metals in high oxidation states. Basic oxides either react with water to give a basic solution or dissolve in strong acid; most basic oxides are oxides of metallic elements. Oxides or hydroxides that are soluble in both acidic and basic solutions are called amphoteric oxides. Most elements whose oxides exhibit amphoteric behavior are located along the diagonal line separating metals and nonmetals in the periodic table. In solutions that contain mixtures of dissolved metal ions, the pH can be used to control the anion concentration needed to selectively precipitate the desired cation.

Contributors and Attributions

- Anonymous

Answers

Exercise 18.7.1

Ag_2CO_3 and Ag_3PO_4

Exercise 18.7.2

$$Cu(OH)_{2(s)} + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l)$$
$$Cu(OH)_{2(s)} + 2OH^-(aq) \rightarrow [Cu(OH)_4]^2_{-(aq)}$$

Exercise 18.7.3

0.018 M H^+

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18.8: Equilibria Involving Complex Ions

Learning Objectives

- To be introduced to complex ions, including ligands.

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 18.8.1. 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 18.8.1: 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 https://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 Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

$$Cu^{2+}(aq) + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)]^{2+}_{(aq)} \quad K_1 \tag{18.8.1}$$
$$[Cu(NH_3)]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_2]^{2+}_{(aq)} \quad K_2 \tag{18.8.2}$$
$$[Cu(NH_3)_2]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_3]^{2+}_{(aq)} \quad K_3 \tag{18.8.3}$$
$$[Cu(NH_3)_3]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \quad K_4 \tag{18.8.4}$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \tag{18.8.5}$$

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:

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = 2.1 \times 10^{13} = K_1K_2K_3K_4 \tag{18.8.6}$$

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 × 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 18.8.1.

*Table 18.8.1: 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}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \diamond [Fe(C_2O_4)_3]^{3-}$	2.0 × 10^{20}

***Reported values are overall formation constants. Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).**

Example 18.8.1

If 12.5 g of $Cu(NO_3)_2•6H_2O$ 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 18.8.5 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 18.8.6) 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 18.8.5. 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:

$$12.5 \cancel{g}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1\ mol}{295.65 \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) = 0.0846\ M \tag{18.8.7}$$

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 $+4x$, 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.

$$\mathbf{Cu^{2+} + 4NH_3 \Diamond [Cu(NH_3)_4]^{2+}}$$

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
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 18.8.6) and assuming that x << 0.0846, which allows us to remove x from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13} \quad (18.8.8)$$

$$x = 2.1 \times 10^{-14} \quad (18.8.9)$$

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 2.1×10^{-14} M.

Exercise 18.8.1

The ferrocyanide ion $\{[Fe(CN)_6]^{4-}\}$ is very stable, with a K_f of 1×10^{35}. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer 2×10^{-6} M

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.

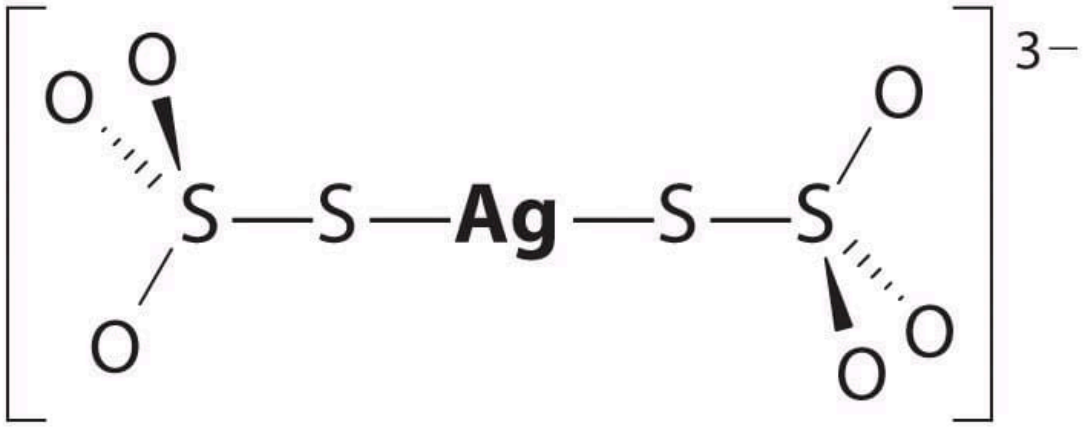
The reaction for the dissolution of silver bromide is as follows:

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)} \quad (18.8.10)$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25°C \quad (18.8.11)$$

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:

$$Ag^+_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{18.8.12}$$

with

$$K_f = 2.9 \times 10^{13} \tag{18.8.13}$$

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:

$$\mathrm{AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \quad } K_{\mathrm{sp}} = 5.35 \times 10^{-13} \tag{18.8.14}$$

$$\mathrm{Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) \quad } K_{\mathrm{f}} = 2.9 \times 10^{13} \tag{18.8.15}$$

$$\mathrm{AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq) \quad } K = K_{\mathrm{sp}}K_{\mathrm{f}} = 15 \tag{18.8.16}$$

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 18.8.2

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 × 10^{-10} for AgCl and K_f = 1.1 × 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,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77\times10^{-10}$$
$$x = 1.33\times10^{-5}$$

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,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77\times10^{-10} = x$$

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:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.77 \times 10^{-10} \tag{18.8.17}$$
$$Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^- \quad K_f = 1.1 \times 10^5 \tag{18.8.18}$$
$$AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^- \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \tag{18.8.19}$$

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,

$$K = \frac{[AgCl_2^-]}{[Cl^-]} = \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} = x$$

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 18.8.2

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

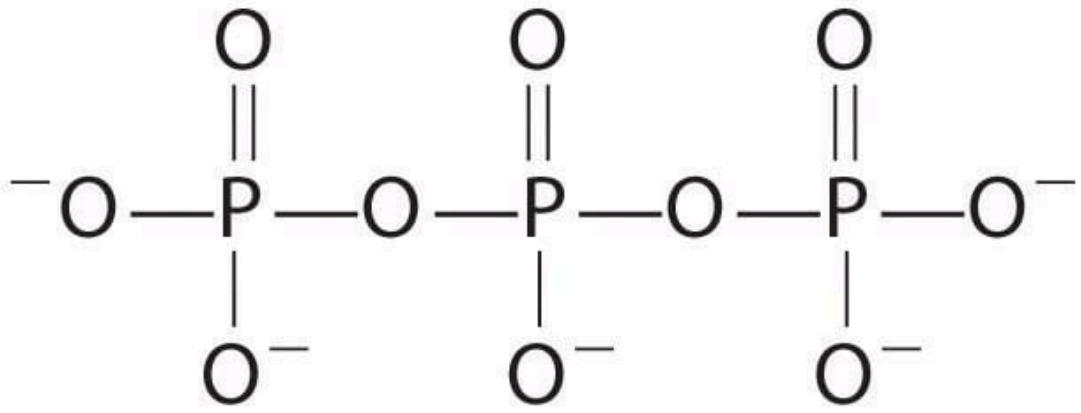
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Solubility of Complex Ions: https://youtu.be/f4pkKDg2XTA

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:



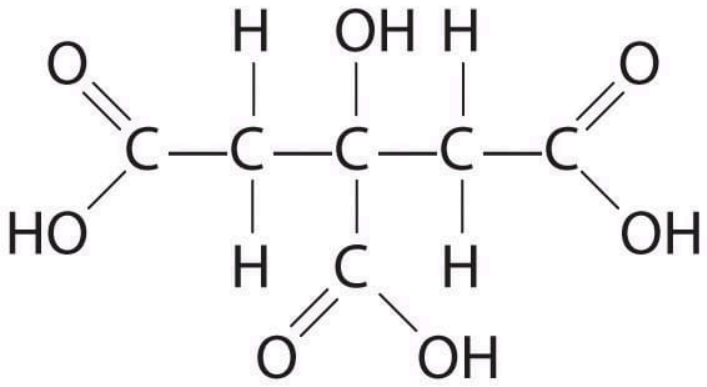
triphosphate

$$Ca^{2+}_{(aq)} + O_3POPO^{4-}_{4(aq)} \rightleftharpoons [Ca(O_3POPO_3)]^{2-}_{(aq)} \tag{18.8.20}$$

with

$$K_f = 4 \times 10^4 \tag{18.8.21}$$

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 18.8.2). 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.

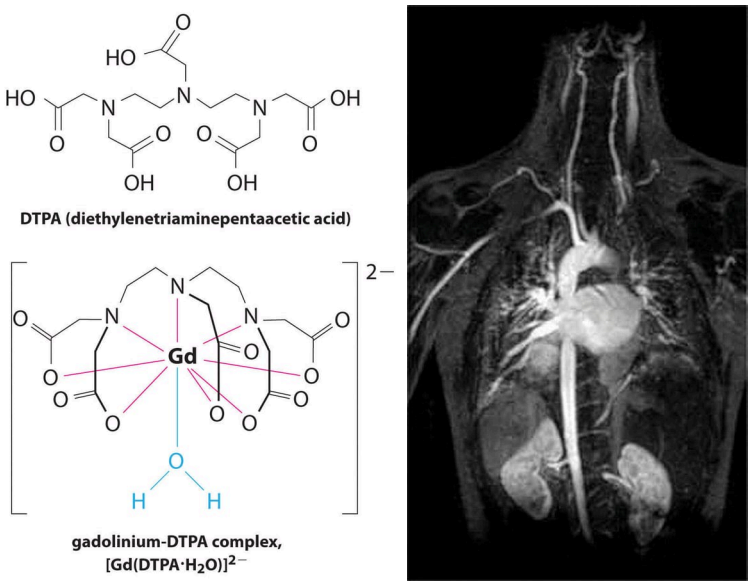


Figure 18.8.2: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Summary

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.

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18.9: Qualitative Cation Analysis

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 18.9.1.

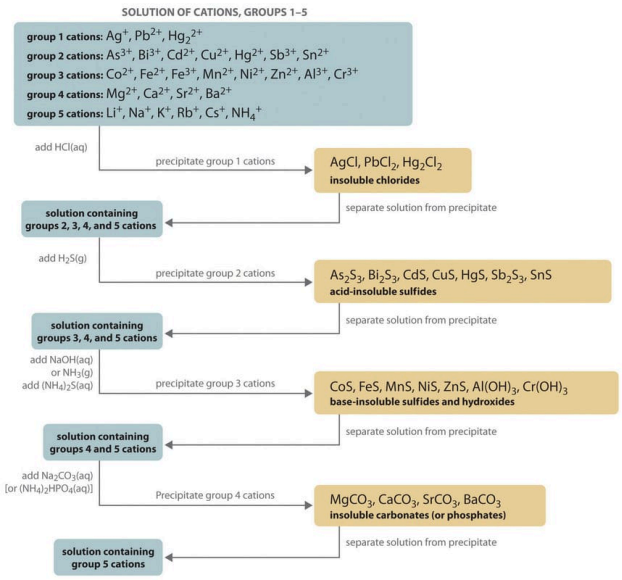


Figure 18.9.1: Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

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 $18.9.2$).



Figure $18.9.2$: 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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19: SPONTANEOUS CHANGE: ENTROPY AND GIBBS ENERGY

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

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19.2: The Concept of Entropy
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19.1: Spontaneity: The Meaning of Spontaneous Change

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).

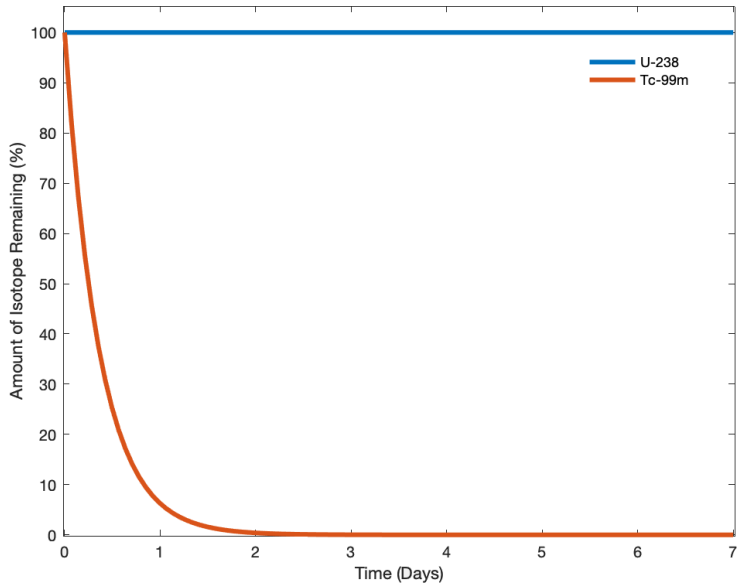


Figure 19.1.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

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.

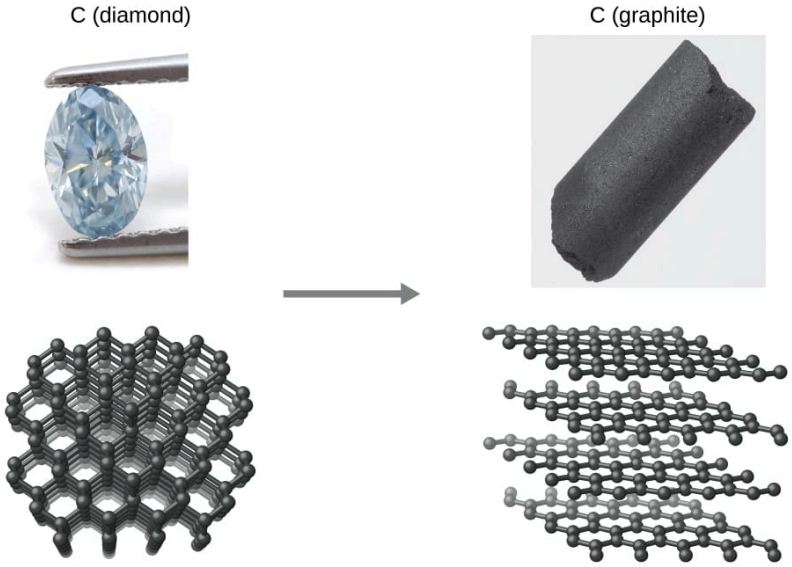


Figure 19.1.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures 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).

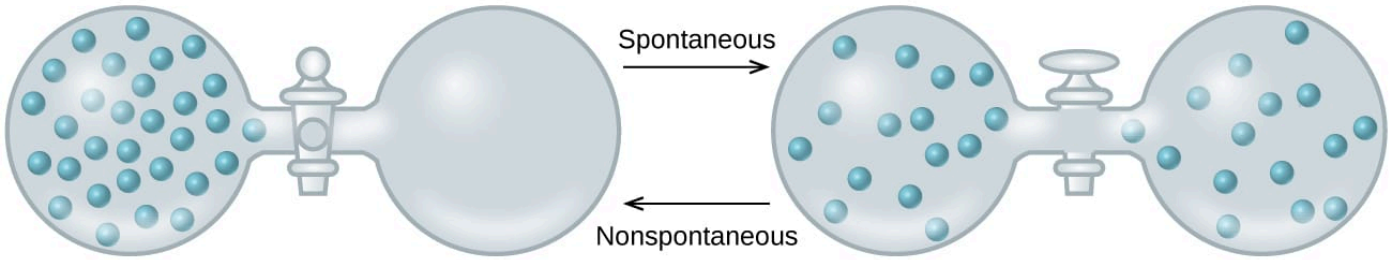


Figure 19.1.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

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: The Concept of Entropy

Learning Objectives

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

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.

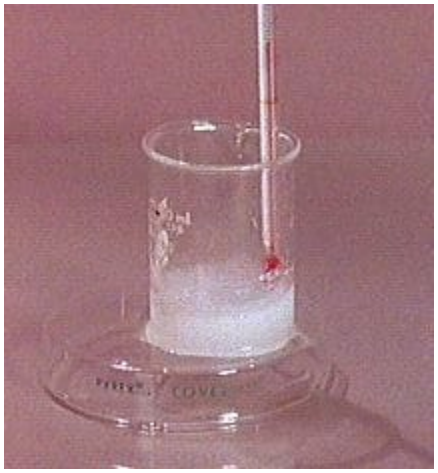


Figure 19.2.1: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes 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 https://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 and Microstates

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 19.2.2) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot's findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). The term reversible process refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

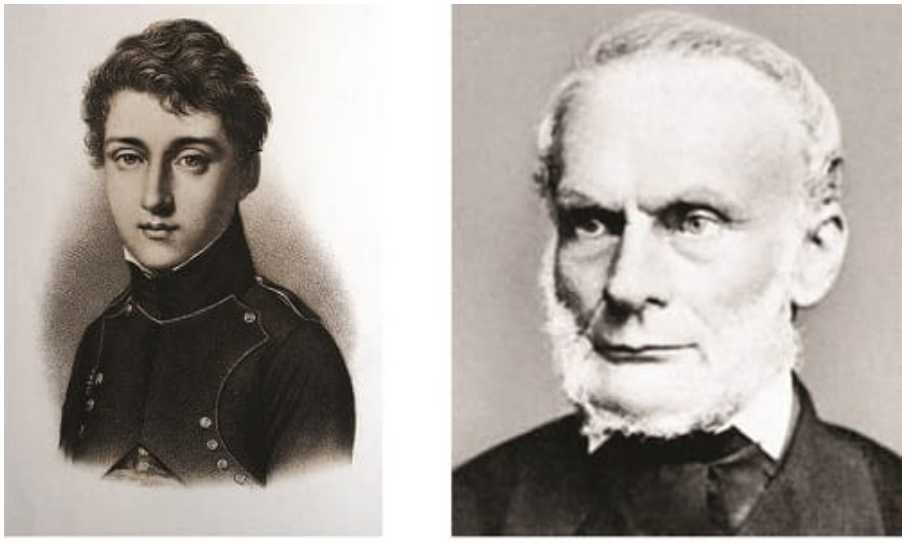


Figure 19.2.2: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{19.2.1}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A microstate (W) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln W \tag{19.2.2}$$

Here k is the Boltzmann constant and has a value of 1.38×10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i} \tag{19.2.3}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure 19.2.3. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

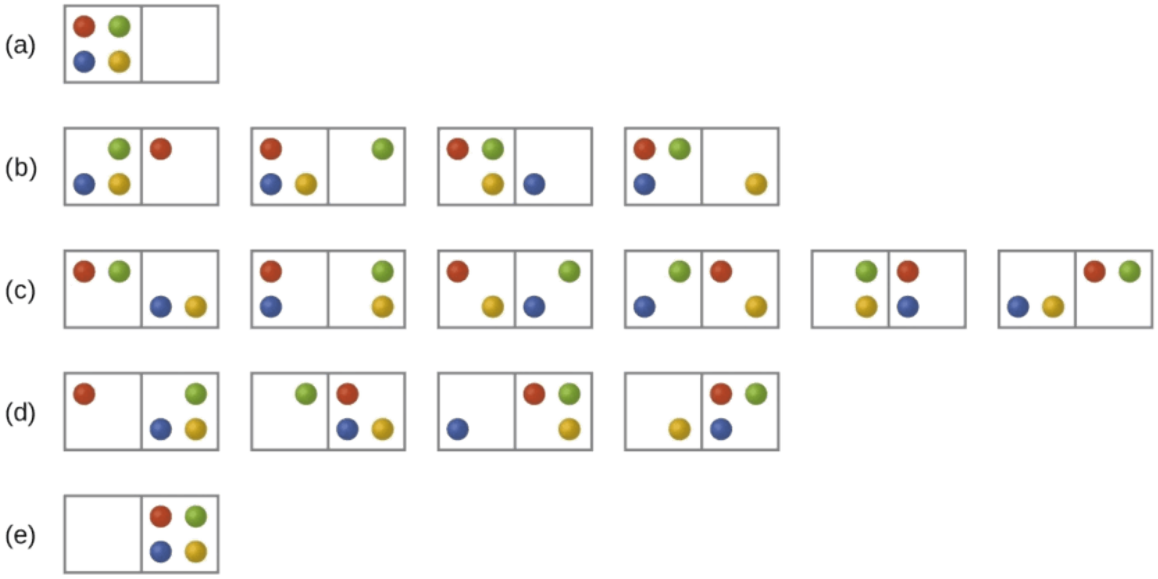


Figure 19.2.3: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$$\frac{6}{16} \text{ or } \frac{3}{8} \tag{19.2.4}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (d), each with a probability of

$$\frac{1}{16} \tag{19.2.5}$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16} \text{ or } \frac{1}{8} \tag{19.2.6}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

The previous description of an ideal gas expanding into a vacuum is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

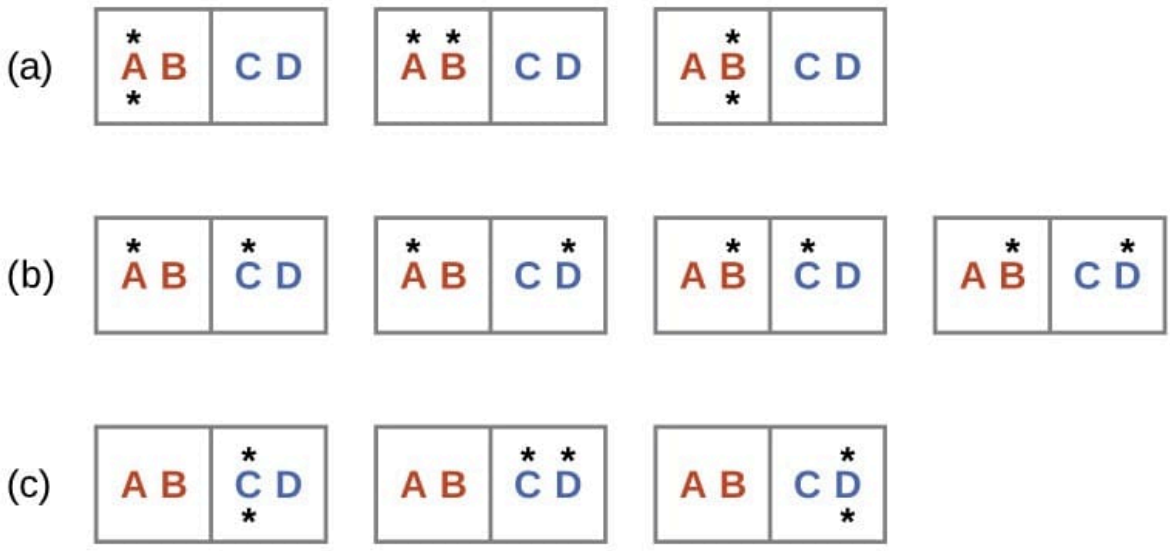


Figure 19.2.4: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as "*") in Figure 19.2.4. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



Solution

We are interested in the following change:

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{W_c}{W_a} = 1.38 \times 10^{-23}\ \text{J/K} \times \ln \frac{6}{1} = 2.47 \times 10^{-23}\ \text{J/K} \tag{19.2.7}$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

Exercise 19.2.1

Consider the system shown in Figure 19.2.3. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer: 0 J/K

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

Entropy: https://youtu.be/dkanY87VsjY

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 19.2.5. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

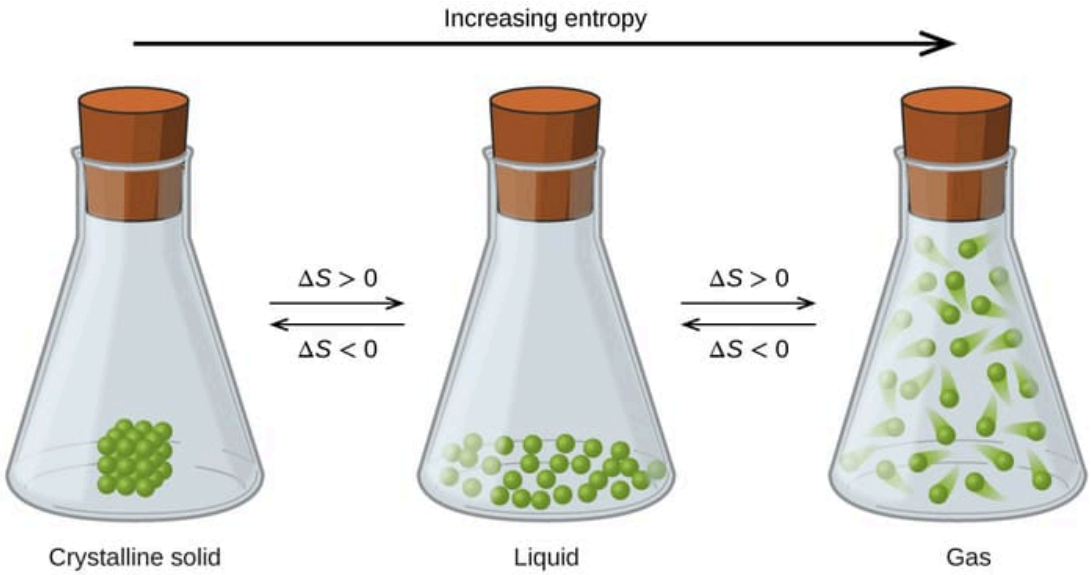


Figure 19.2.5: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure 19.2.6).

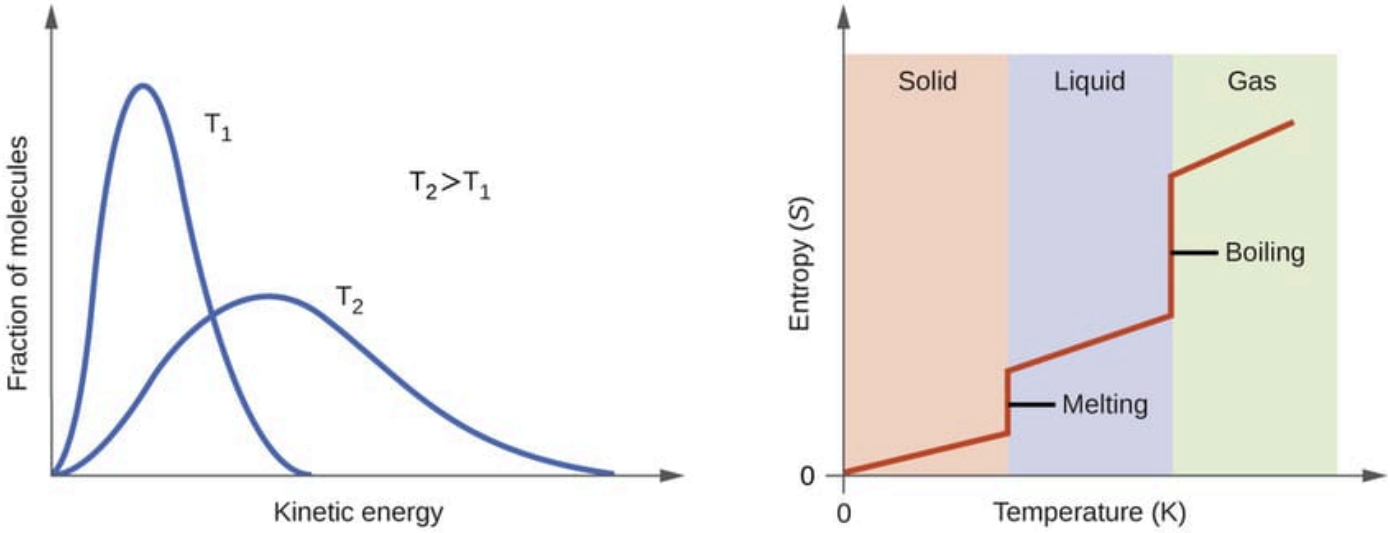


Figure 19.2.6: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

The entropy of a substance is influenced by structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example .

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature $\longrightarrow$ one mole liquid water at 50 °C
b. $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$
c. $\mathrm{C_6H_6}(l) + \frac{15}{2}\mathrm{O_2}(g) \longrightarrow 6\,\mathrm{CO_2}(g) + 3\,\mathrm{H_2O}(l)$
d. $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

Solution

a. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

Exercise 19.2.2

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $\mathrm{NaNO_3}(s) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$
b. the freezing of liquid water
c. $\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g)$
d. $\mathrm{CaCO}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

Answer:

(a) Positive; The solid dissolves to give an increase of mobile ions in solution. (b) Negative; The liquid becomes a more ordered solid. (c) Positive; The relatively ordered solid becomes a gas. (d) Positive; There is a net production of one mole of gas.

Note

Entropy (S) is a thermodynamic property of all substances. 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 $\Delta S_{soln} > 0$.

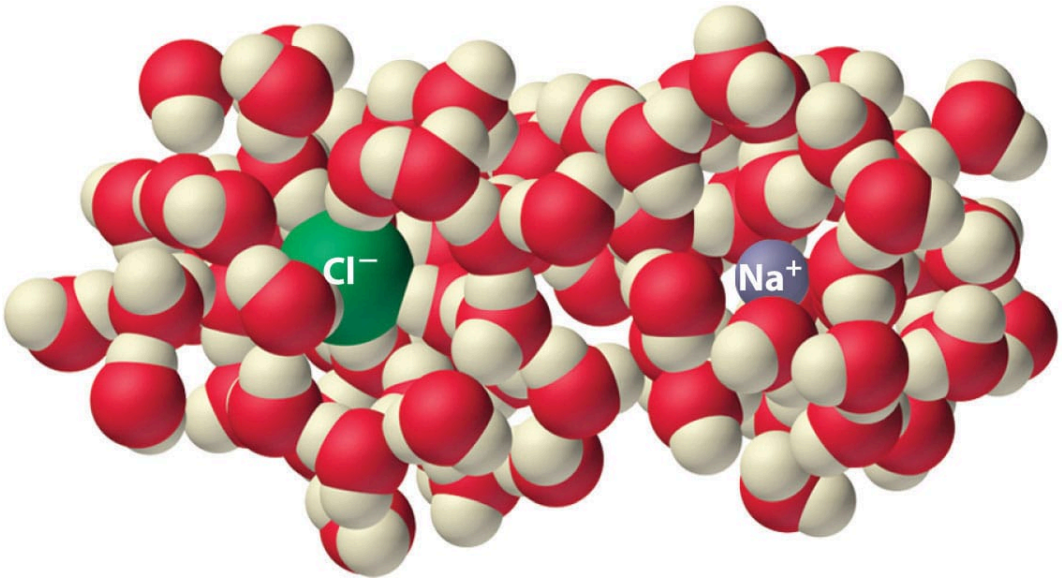


Figure 19.2.7 The Effect of Solution Formation on Entropy

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 19.2.3

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 19.2.3

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. 1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)
b. 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)

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

$$\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev} \tag{19.2.8}$$

Note

Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$.

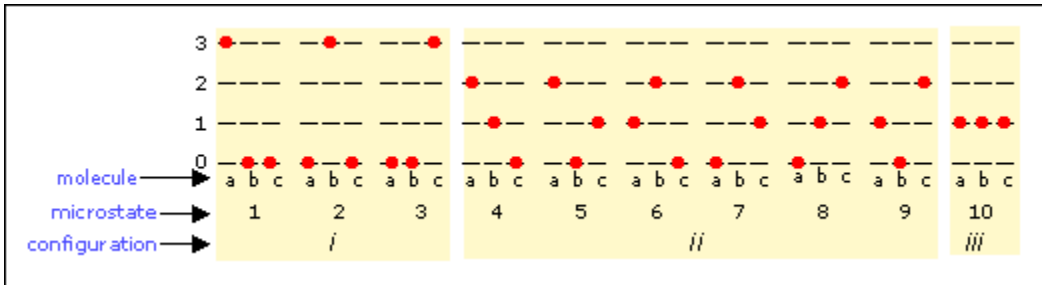
In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

Quantum states and Energy Spreading

At the atomic and molecular level, all energy is *quantized*; each particle possesses discrete states of kinetic energy and is able to accept thermal energy only in packets whose values correspond to the energies of one or more of these states. Polyatomic molecules can store energy in rotational and vibrational motions, and all molecules (even monatomic ones) will possess translational kinetic energy (thermal energy) at all temperatures above absolute zero. The energy difference between adjacent translational states is so minute that translational kinetic energy can be regarded as *continuous* (non-quantized) for most practical purposes.

The number of ways in which thermal energy can be distributed amongst the allowed states within a collection of molecules is easily calculated from simple statistics, but we will confine ourselves to an example here. Suppose that we have a system consisting of three molecules and three quanta of energy to share among them. We can give all the kinetic energy to any one molecule, leaving the others with none, we can give two units to one molecule and one unit to another, or we can share out the

energy equally and give one unit to each molecule. All told, there are ten possible ways of distributing three units of energy among three identical molecules as shown here:



Each of these ten possibilities represents a distinct *microstate* that will describe the system at any instant in time. Those microstates that possess identical distributions of energy among the accessible quantum levels (and differ only in which particular molecules occupy the levels) are known as **configurations**. Because all microstates are equally probable, the probability of any one configuration is proportional to the number of microstates that can produce it. Thus in the system shown above, the configuration labeled *ii* will be observed 60% of the time, while *iii* will occur only 10% of the time.

As the number of molecules and the number of quanta increases, the number of accessible microstates grows explosively; if 1000 quanta of energy are shared by 1000 molecules, the number of available microstates will be around 10^{600}— a number that greatly exceeds the number of atoms in the observable universe! The number of possible configurations (as defined above) also increases, but in such a way as to greatly reduce the probability of all but the most probable configurations. Thus for a sample of a gas large enough to be observable under normal conditions, only a single configuration (energy distribution amongst the quantum states) need be considered; even the second-most-probable configuration can be neglected.

The bottom line: any collection of molecules large enough in numbers to have chemical significance will have its therrmal energy distributed over an unimaginably large number of microstates. The number of microstates increases exponentially as more energy states ("configurations" as defined above) become accessible owing to

- Addition of energy quanta (higher temperature),
- Increase in the number of molecules (resulting from dissociation, for example).
- the volume of the system increases (which decreases the spacing between energy states, allowing more of them to be populated at a given temperature.)

Key Concepts and 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.

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{19.2.9}$$

Entropy (S) is 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. Entropy (S) may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system.

For a given substance, $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$ in a given physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions may be reliably predicted.

Key Equations

- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $S = k \ln W$

- $\Delta S = k \ln \frac{W_\mathrm{f}}{W_\mathrm{i}}$

Glossary

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

microstate (*W*)
: possible configuration or arrangement of matter and energy within a system

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

Contributors and Attributions

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19.3: Evaluating Entropy and Entropy Changes

Learning Objectives

- To use thermodynamic cycles to calculate changes in entropy.

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 19.3.1). 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.

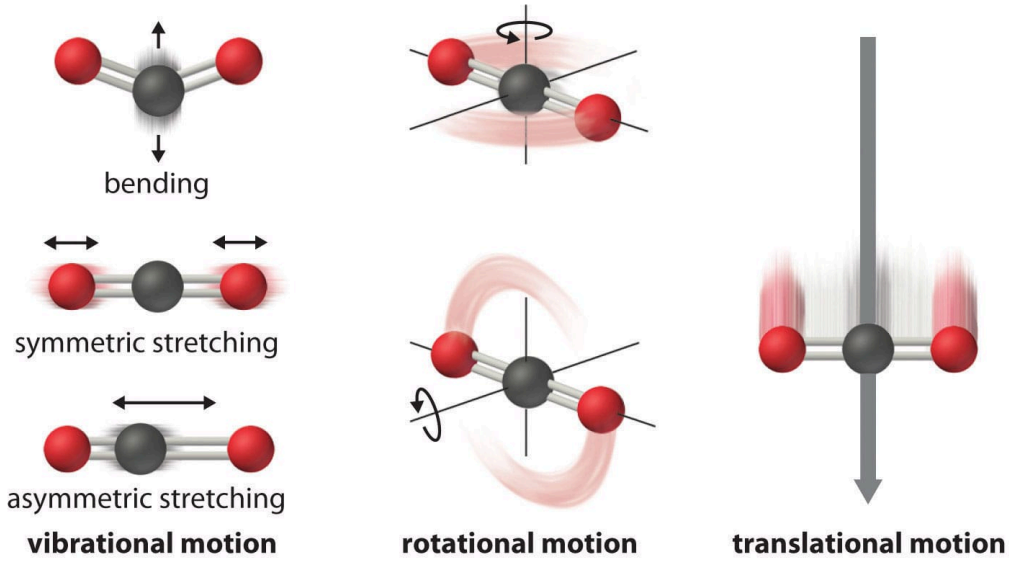


Figure 19.3.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

Third Law of Thermodynamics

The entropy of any perfectly ordered, crystalline substance at absolute zero is *zero*.

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.

Calculating ΔS from Standard Molar Entropy Values

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.

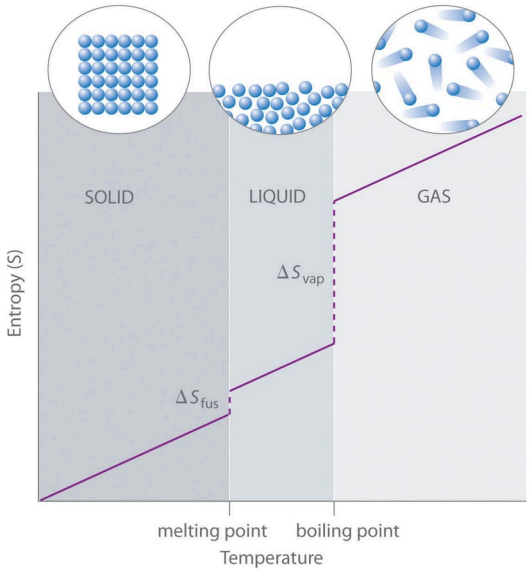


Figure 19.3.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (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)]*
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

Note

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.

Note

ΔS° for a reaction can be calculated from absolute entropy values using the same "products minus reactants" rule used to calculate ΔH°.

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 19.3.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

Example 19.3.1

Use the data in Table 19.3.1 to calculate ΔS° for the 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 19.3.1. 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:

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$$

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:

$$\Delta S^\circ_{\text{rxn}} = \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants}) \tag{19.3.1}$$

$$= [8S^\circ(CO_2) + 9S^\circ(H_2O)] - [S^\circ(C_8H_{18}) + \frac{25}{2}S^\circ(O_2)] \tag{19.3.2}$$

$$= \{[8 \text{ mol } CO_2 \times 213.8 \text{ J/(mol} \cdot \text{K)}] + [9 \text{ mol } H_2O \times 188.8 \text{ J/(mol} \cdot \text{K)}]\} \tag{19.3.3}$$

$$- \left\{[1 \text{ mol } C_8H_{18} \times 329.3 \text{ J/(mol} \cdot \text{K)}] + \left[\frac{25}{2} \text{ mol } O_2 \times 205.2 \text{ J/(mol} \cdot \text{K)}\right]\right\} \tag{19.3.4}$$

$$= 515.3 \text{ J/K} \tag{19.3.5}$$

ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise 19.3.1

Use the data in Table 19.3.1 to calculate ΔS° for the reaction of H_2(g) with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer: −361.1 J/K

Calculating ΔS from Thermodynamic Cycles

We can also calculate a change in entropy using a thermodynamic cycle. As you learned previously, the molar heat capacity (C_p) is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant pressure. Similarly, C_v is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant volume. The increase in entropy with increasing temperature in Figure 19.3.2 is approximately proportional to the heat capacity of the substance.

Recall that the entropy change (ΔS) is related to heat flow (q_{rev}) by $\Delta S = q_{rev}/T$. Because $q_{rev} = nC_p\Delta T$ at constant pressure or $nC_v\Delta T$ at constant volume, where n is the number of moles of substance present, the change in entropy for a substance whose temperature changes from T_1 to T_2 is as follows:

$$\Delta S = \frac{q_{\text{rev}}}{T} = nC_{\text{p}}\frac{\Delta T}{T} \quad (\text{constant pressure}) \tag{19.3.6}$$

As you will discover in more advanced math courses than is required here, it can be shown that this is equal to the following:For a review of natural logarithms, see Essential Skills 6 in Chapter 11.

$$\Delta S = nC_{\text{p}} \ln \frac{T_2}{T_1} \quad (\text{constant pressure}) \tag{19.3.7}$$

Similarly,

$$\Delta S = nC_{\text{v}} \ln \frac{T_2}{T_1} \quad (\text{constant volume}) \tag{19.3.8}$$

Thus we can use a combination of heat capacity measurements (Equation 18.20 or Equation 18.21) and experimentally measured values of enthalpies of fusion or vaporization if a phase change is involved (Equation 18.18) to calculate the entropy change corresponding to a change in the temperature of a sample.

We can use a thermodynamic cycle to calculate the entropy change when the phase change for a substance such as sulfur cannot be measured directly. As noted in the exercise in Example 6, elemental sulfur exists in two forms (part (a) in Figure 19.3.3): an orthorhombic form with a highly ordered structure (S_α) and a less-ordered monoclinic form (S_β). The orthorhombic (α) form is more stable at room temperature but undergoes a phase transition to the monoclinic (β) form at temperatures greater than 95.3°C (368.5 K). The transition from S_α to S_β can be described by the thermodynamic cycle shown in part (b) in Figure 19.3.3, in which liquid sulfur is an intermediate. The change in entropy that accompanies the conversion of liquid sulfur to S_β ($-\Delta S_{fus(\beta)} = \Delta S_3$ in the cycle) cannot be measured directly. Because entropy is a state function, however, ΔS_3 can be calculated from the overall entropy change (ΔS_t) for the S_α–S_β transition, which equals the sum of the ΔS values for the steps in the thermodynamic cycle, using Equation 18.20 and tabulated thermodynamic parameters (the heat capacities of S_α and S_β, $\Delta H_{fus(\alpha)}$, and the melting point of S_α.)

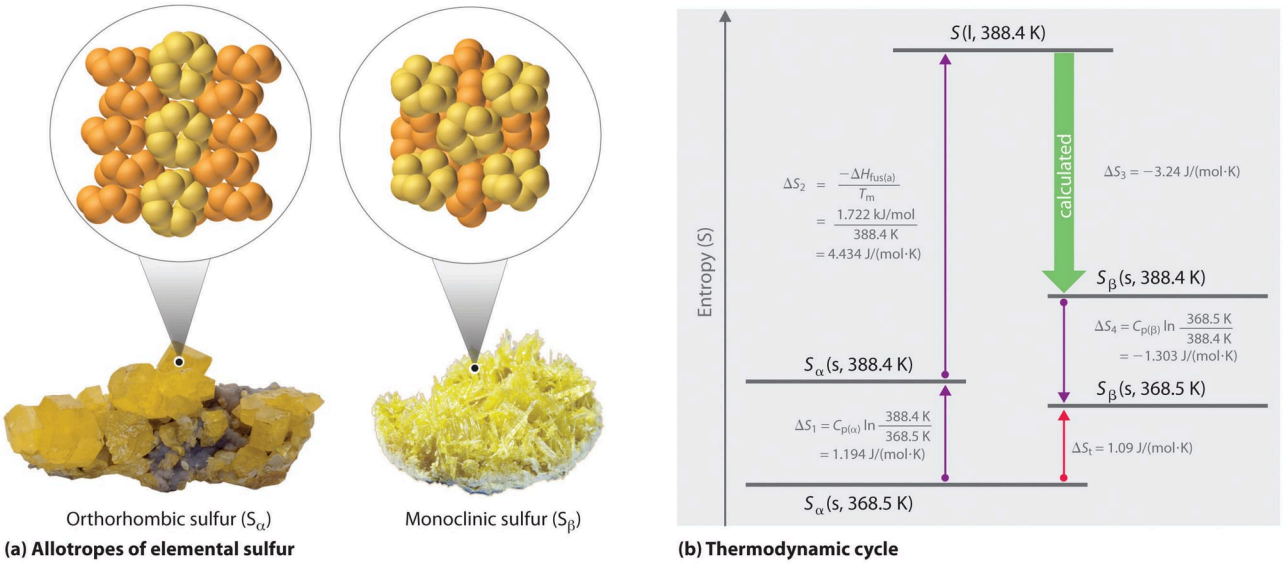


Figure 19.3.3: Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other(a) Orthorhombic sulfur (S_α) has a highly ordered structure in which the S_8 rings are stacked in a "crankshaft" arrangement. Monoclinic sulfur (S_β) is also composed of S_8 rings but has a less-ordered structure. (b) At 368.5 K, S_α undergoes a phase transition to S_β. Although ΔS_3 cannot be measured directly, it can be calculated using the values shown in this thermodynamic cycle.

If we know the melting point of S_α (T_m = 115.2°C = 388.4 K) and ΔS_t for the overall phase transition [calculated to be 1.09 J/(mol•K) in the exercise in Example 6], we can calculate ΔS_3 from the values given in part (b) in Figure 19.3.3 where $C_{p(\alpha)}$ = 22.70 J/mol•K and $C_{p(\beta)}$ = 24.77 J/mol•K (subscripts on ΔS refer to steps in the cycle):

$$\Delta S_t = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 \tag{19.3.9}$$

$$1.09\ \text{J/(mol} \cdot \text{K)} = C_{p(\alpha)} \ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_{fus}}{T_m} + \Delta S_3 + C_{p(\beta)} \ln\left(\frac{T_4}{T_3}\right) \tag{19.3.10}$$

$$= 22.70\ \text{J/(mol} \cdot \text{K)} \ln\left(\frac{388.4}{368.5}\right) + \left(\frac{1.722\ \text{kJ/mol}}{388.4\ \text{K}} \times 1000\ \text{J/kJ}\right) \tag{19.3.11}$$

$$+ \Delta S_3 + 24.77\ \text{J/(mol} \cdot \text{K)} \ln\left(\frac{368.5}{388.4}\right) \tag{19.3.12}$$

$$= [1.194\ \text{J/(mol} \cdot \text{K)}] + [4.434\ \text{J/(mol} \cdot \text{K)}] + \Delta S_3 + [-1.303\ \text{J/(mol} \cdot \text{K)}] \tag{19.3.13}$$

Solving for ΔS_3 gives a value of –3.24 J/(mol•K). As expected for the conversion of a less ordered state (a liquid) to a more ordered one (a crystal), ΔS_3 is negative.

How are Entropies Measured

The *absolute entropy* of a substance at any temperature above 0 K must be determined by calculating the increments of heat *q* required to bring the substance from 0 K to the temperature of interest, and then summing the ratios *q*/*T*. Two kinds of experimental measurements are needed:

1. The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with melting, for example, is just $\Delta H_{fusion}/T_m$.
2. The **heat capacity** *C* of a phase expresses the quantity of heat required to change the temperature by a small amount ΔT, or more precisely, by an infinitesimal amount dT. Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities $C\ dT/T$ for each increment of temperature dT. This is of course just the integral

$$S_{0\rightarrow T^o} = \int_0^{T^o} \frac{C_p}{T} dt \tag{19.3.14}$$

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of C on T be used in the above integral in place of a constant C.

$$S_{0\rightarrow T^o} = \int_0^{T^o} \frac{C_p(T)}{T} dt \tag{19.3.15}$$

When this is not known, one can take a series of heat capacity measurements over narrow temperature increments ΔT and measure the area under each section of the curve.

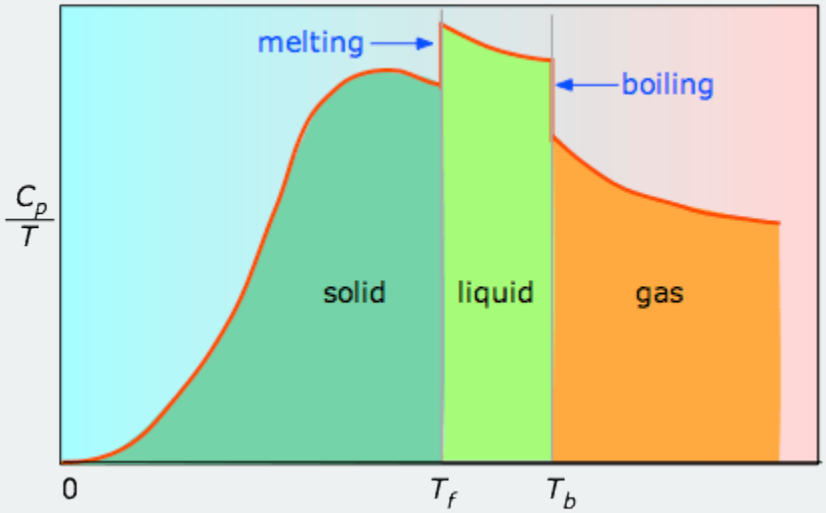


Figure 19.3.4: Heat capitity/temperature as a function of temperature

The area under each section of the plot represents the entropy change associated with heating the substance through an interval ΔT. To this must be added the enthalpies of melting, vaporization, and of any solid-solid phase changes. Values of C_p for temperatures near zero are not measured directly, but can be estimated from quantum theory.

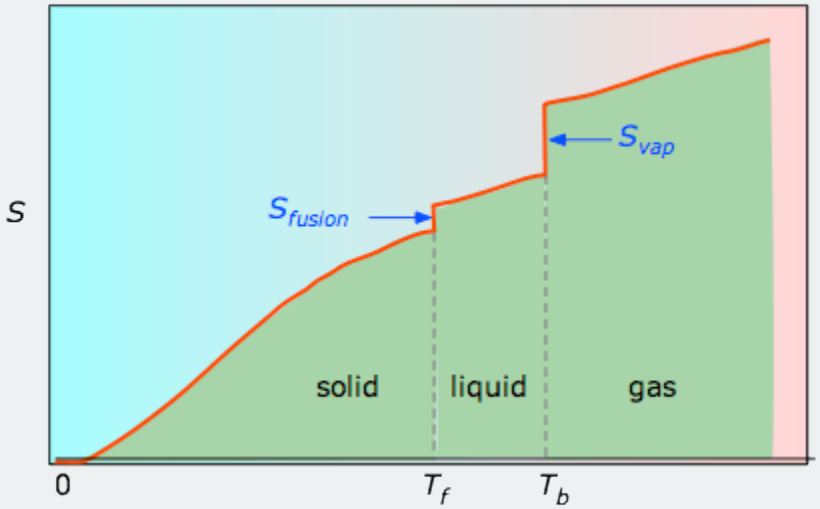


Figure 19.3.5: Molar entropy as a function of temperature

The cumulative areas from 0 K to any given temperature (taken from the experimental plot on the left) are then plotted as a function of T, and any phase-change entropies such as $S_{vap} = H_{vap} / T_b$ are added to obtain the absolute entropy at temperature T.

Summary

- Entropy changes can be calculated using the “products minus reactants” rule or from a combination of heat capacity measurements and measured values of enthalpies of fusion or vaporization.

The third law of thermodynamics states that the entropy of any perfectly ordered, crystalline substance at absolute zero is zero. At temperatures greater than absolute zero, entropy has a positive value, which allows us to measure the absolute entropy of a substance. Measurements of the heat capacity of a substance and the enthalpies of fusion or vaporization can be used to calculate the changes in entropy that accompany a physical change. The entropy of 1 mol of a substance at a standard temperature of 298 K is its standard molar entropy ($S°$). We can use the “products minus reactants” rule to calculate the standard entropy change ($\Delta S°$) for a reaction using tabulated values of $S°$ for the reactants and the products.

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19.4: Criteria for Spontaneous Change: The Second Law of Thermodynamics

Learning Objectives

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{19.4.1}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \tag{19.4.2}$$

   The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*
2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \tag{19.4.3}$$

   The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The temperature difference between the objects is infinitesimally small, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the heat flow is thermodynamically reversible. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table 19.4.1.

Table 19.4.1: The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	reversible (system is at equilibrium)

Definition: The Second Law of Thermodynamics

All spontaneous changes cause an increase in the entropy of the universe.

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \tag{19.4.4}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 19.4.1.

Will Ice Spontaneously Melt?

The entropy change for the process

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at –10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = –6.00 kJ.

At –10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{263.15\ \text{K}} = -0.7\ \text{J/K}\end{aligned}$$

S_{univ} < 0, so melting is nonspontaneous (*not* spontaneous) at –10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

$$= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{283.15\ \text{K}} = +0.9\ \text{J/K}$$

S_{univ} > 0, so melting *is* spontaneous at 10.00 °C.

Exercise 19.4.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

Answer:

Entropy is a state function, and freezing is the opposite of melting. At –10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, –0.9 J/K.

Gibbs Energy and Changes of Gibbs Energy

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that we must determine the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the Gibbs free energy change (*G*) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS \tag{19.4.5}$$

Free energy is a state function, and at constant temperature and pressure, the standard free energy change (ΔG°) may be expressed as the following:

$$\Delta G = \Delta H - T\Delta S \tag{19.4.6}$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.) We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T} \tag{19.4.7}$$

The first law requires that qsurr = −qsys, and at constant pressure qsys = ΔH, and so this expression may be rewritten as the following:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T} \tag{19.4.8}$$

ΔH is the enthalpy change of the system. Multiplying both sides of this equation by −T, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S \tag{19.4.9}$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}} \tag{19.4.10}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table $19.4.2$ expands on Table $19.4.2$ and summarizes the relation between the spontaneity of a process and the arithmetic signs of ΔG and ΔS indicators.

Table $19.4.2$*: Relation between Process Spontaneity and Signs of Thermodynamic Properties*

$\Delta S_{univ} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{univ} = 0$	$\Delta G = 0$	reversible (at equilibrium)

. 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.

Gibbs energy is a state function, so its value depends only on the conditions of the initial and final states of the system that have undergone some change. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation as demonstrated

in Example 19.4.1.

Label '\({19{.}4{.}\eatSpaces{7} \endSpaces}\)' multiply defined

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 Definition of Gibbs Free Energy: https://youtu.be/iuWkcHUh-1o

Example 19.4.2: Evaluation of ΔG°

Change from ΔH° and ΔS° Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

Solution

The process of interest is the following:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ$$

From Appendix G, here is the data:

Substance	$\Delta H^\circ_f (k\,\mathrm{J/mol})$	$S^\circ_{298} (\mathrm{J/K{\cdot}mol})$
$H_2O(l)$	−286.83	70.0
$H_2O(g)$	−241.82	188.8

Combining at 298 K:

$$\Delta H^\circ = \Delta H^\circ_{298} = \Delta H^\circ_f(\mathrm{H_2O}(g)) - \Delta H^\circ_f(\mathrm{H_2O}(l))$$
$$= [-241.82\ \mathrm{kJ} - (-285.83)]\ \mathrm{kJ/mol} = 44.01\ \mathrm{kJ/mol}$$

$$\Delta S^\circ = \Delta S^\circ_{298} = S^\circ_{298}(\mathrm{H_2O}(g)) - S^\circ_{298}(\mathrm{H_2O}(l))$$
$$= 188.8\ \mathrm{J/mol \cdot K} - 70.0\ \mathrm{J/K} = 118.8\ \mathrm{J/mol \cdot K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Converting everything into kJ and combining at 298 K:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ$$

$$= 44.01\ \mathrm{kJ/mol} - (298\ \mathrm{K} \times 118.8\ \mathrm{J/mol \cdot K}) \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}$$

$$44.01\ \text{kJ/mol} - 35.4\ \text{kJ/mol} = 8.6\ \text{kJ/mol}$$

At 298 K (25 °C) $\Delta G^\circ_{298} > 0$, and so boiling is nonspontaneous (not spontaneous).

Exercise 19.4.2

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

$$C_2H_6(g) \longrightarrow H_2(g) + C_2H_4(g)$$

Answer:

$\Delta G^\circ_{298} = 102.0\ \text{kJ/mol}$; the reaction is nonspontaneous (not spontaneous) at 25 °C.

Free energy changes may also use the standard free energy of formation (ΔG°_f), for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, (ΔG°_f) is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$mA + nB \longrightarrow xC + yD, \tag{19.4.11}$$

the standard free energy change at room temperature may be calculated as

$$\Delta G^\circ_{298} = \Delta G° = \sum \nu \Delta G^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants}) \tag{19.4.12}$$

$$= [x\Delta G^\circ_f(C) + y\Delta G^\circ_f(D)] - [m\Delta G^\circ_f(A) + n\Delta G^\circ_f(B)]. \tag{19.4.13}$$

Example 19.4.3: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

$$HgO(s,\ \text{yellow}) \longrightarrow Hg(l) + \frac{1}{2}O_2(g)$$

Calculate the standard free energy change at room temperature, ΔG°_{298}, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in Appendix G and are shown here.

Compound	ΔG°_f (kJ/mol)	ΔH°_f (kJ/mol)	S°_{298} (J/K·mol)
HgO (s, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
O_2(*g*)	0	0	205.2

(a) Using free energies of formation:

$$\Delta G^\circ_{298} = \sum \nu G S^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta G^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta G^\circ_{298}\text{O}_2(g)\right] - 1\Delta G^\circ_{298}\text{HgO}(s,\text{ yellow})$$

$$= \left[1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})\right] - 1\text{ mol}(-58.43\text{ kJ/mol}) = 58.43\text{ kJ/mol}$$

(b) Using enthalpies and entropies of formation:

$$\Delta H^\circ_{298} = \sum \nu \Delta H^\circ_{298}(\text{products}) - \sum \nu \Delta H^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta H^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta H^\circ_{298}\text{O}_2(g)\right] - 1\Delta H^\circ_{298}\text{HgO}(s,\text{ yellow})$$

$$= [1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})] - 1\text{ mol}(-90.46\text{ kJ/mol}) = 90.46\text{ kJ/mol}$$

$$\Delta S^\circ_{298} = \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta S^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta S^\circ_{298}\text{O}_2(g)\right] - 1\Delta S^\circ_{298}\text{HgO}(s,\text{ yellow})$$

$$= \left[1\text{ mol}(75.9\text{ J/mol K}) + \frac{1}{2}\text{mol}(205.2\text{ J/mol K})\right] - 1\text{ mol}(71.13\text{ J/mol K}) = 107.4\text{ J/mol K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 90.46\text{ kJ} - 298.15\text{ K} \times 107.4\text{ J/K} \cdot \text{mol} \times \frac{1\text{ kJ}}{1000\text{ J}}$$

$$\Delta G^\circ = (90.46 - 32.01)\text{ kJ/mol} = 58.45\text{ kJ/mol}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (not spontaneous) at room temperature.

Exercise 19.4.3

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Appendix G). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

$$\text{C}_2\text{H}_4(g) \longrightarrow \text{H}_2(g) + \text{C}_2\text{H}_2(g)$$

Answer

–141.5 kJ/mol, nonspontaneous

Key Concepts and Summary

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{univ} > 0$. If $\Delta S_{univ} < 0$, the process is nonspontaneous, and if $\Delta S_{univ} = 0$, the system is at equilibrium. Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium. A number of approaches to the computation of free energy changes are possible.

Key Equations

- $\Delta S^\circ = \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants})$

- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$
- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G^\circ + RT \ln Q$
- $\Delta G^\circ = -RT \ln K$

Glossary

Gibbs free energy change (*G*)
: thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in *G*

standard free energy change (ΔG°)
: 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 $(\Delta G_{\text{f}}^\circ)$
: change in free energy accompanying the formation of one mole of substance from its elements in their standard states

second law of thermodynamics
: entropy of the universe increases for a spontaneous process

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}°

Contributors and Attributions

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19.5: Standard Gibbs Energy Change, ΔG°

Learning Objectives

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products

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.

The criterion for predicting spontaneity is based on Δ*G*, 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*. Under standad conditions Equation 19.5.2 is then expressed at

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{19.5.3}$$

Since G is a state function, ΔG^o can be obtained from the *standard free-energy of formation* values in Table T1 (or T2) via the similar relationship used to calculate other state functions like ΔH^o and ΔS^o:

$$\Delta G^o = \sum n\Delta G^o_f\,(products) - \sum m\Delta G^o_f\,(reactants) \tag{19.5.4}$$

Example 19.5.1: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

$$\mathrm{HgO}(s,\text{ yellow}) \longrightarrow \mathrm{Hg}(l) + \frac{1}{2}\mathrm{O_2}(g)$$

Calculate the standard free energy change at room temperature, ΔG°_{298}, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions? The required data are available in Table T1 .

Solution

The required data are available in Table T1 and are shown here.

Compound	ΔG°_f (kJ/mol)	ΔH°_f (kJ/mol)	S°_{298} (J/K·mol)
HgO (s, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
O_2(*g*)	0	0	205.2

(a) Using free energies of formation:

$$\Delta G^\circ_{298} = \sum \nu G S^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta G^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta G^\circ_{298}\text{O}_2(g)\right] - 1\Delta G^\circ_{298}\text{HgO}(s,\text{ yellow})$$

$$= \left[1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})\right] - 1\text{ mol}(-58.43\text{ kJ/mol}) = 58.43\text{ kJ/mol}$$

(b) Using enthalpies and entropies of formation:

$$\Delta H^\circ_{298} = \sum \nu \Delta H^\circ_{298}(\text{products}) - \sum \nu \Delta H^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta H^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta H^\circ_{298}\text{O}_2(g)\right] - 1\Delta H^\circ_{298}\text{HgO}(s,\text{ yellow})$$

$$= [1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})] - 1\text{ mol}(-90.46\text{ kJ/mol}) = 90.46\text{ kJ/mol}$$

$$\Delta S^\circ_{298} = \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta S^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta S^\circ_{298}\text{O}_2(g)\right] - 1\Delta S^\circ_{298}\text{HgO}(s,\text{ yellow})$$

$$= \left[1\text{ mol}(75.9\text{ J/mol K}) + \frac{1}{2}\text{mol}(205.2\text{ J/mol K})\right] - 1\text{ mol}(71.13\text{ J/mol K}) = 107.4\text{ J/mol K}$$

Now use these values in Equation 19.5.3 to get ΔG^o:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 90.46\text{ kJ} - 298.15\text{ K} \times 107.4\text{ J/K} \cdot \text{mol} \times \frac{1\text{ kJ}}{1000\text{ J}}$$

$$\Delta G^\circ = (90.46 - 32.01)\text{ kJ/mol} = 58.45\text{ kJ/mol}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (not spontaneous) at room temperature (since $\Delta G^o > 0$.

Exercise 19.5.1

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Appendix G). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

$$\text{C}_2\text{H}_4(g) \longrightarrow \text{H}_2(g) + \text{C}_2\text{H}_2(g)$$

Answer

–141.5 kJ/mol, nonspontaneous

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Calculating Gibbs Free Energy (Grxn) for a Reaction: https://youtu.be/wmreE6zeFQo

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19.6: Gibbs Energy Change and Equilibrium

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.
- The sign of the standard free energy change $\Delta G°$ of a chemical reaction determines whether the reaction will tend to proceed in the forward or reverse direction.
- Similarly, the relative signs of $\Delta G°$ and $\Delta S°$ determine whether the spontaniety of a chemical reaction will be affected by the temperature, and if so, in what way.

ΔG is meaningful only for changes in which the temperature and pressure remain constant. These are the conditions under which most reactions are carried out in the laboratory; the system is usually open to the atmosphere (constant pressure) and we begin and end the process at room temperature (after any heat we have added or which is liberated by the reaction has dissipated.) The importance of the Gibbs function can hardly be over-stated: **it serves as the single master variable that determines whether a given chemical change is thermodynamically possible.** Thus if the free energy of the reactants is greater than that of the products, the entropy of the world will increase when the reaction takes place as written, and so the reaction will tend to take place spontaneously. Conversely, if the free energy of the products exceeds that of the reactants, then the reaction will not take place in the direction written, but it will tend to proceed in the reverse direction.

Temperature Dependence to ΔG

In a spontaneous change, Gibbs energy always decreases and never increases. This of course reflects the fact that the entropy of the world behaves in the exact opposite way (owing to the negative sign in the $T\Delta S$ term).

$$H_2O_{(l)} \rightarrow H_2O_{(s)} \tag{19.6.1}$$

water below its freezing point undergoes a decrease in its entropy, but the heat released into the surroundings more than compensates for this, so the entropy of the world increases, the free energy of the H_2O diminishes, and the process proceeds spontaneously.

Note

In a spontaneous change, Gibbs energy **always** decreases and never increases.

An important consequence of the one-way downward path of the free energy is that once it reaches its minimum possible value, all net change comes to a halt. This, of course, represents the state of chemical equilibrium. These relations are nicely summarized as follows:

- $\Delta G < 0$: reaction can spontaneously proceed to the right:

$$A \rightarrow B \tag{19.6.2}$$

- $\Delta G > 0$: reaction can spontaneously proceed to the left:

$$A \leftarrow B \tag{19.6.3}$$

- $\Delta G = 0$: the reaction is at equilibrium; the quantities of [A] and [B] will not change

Recall the condition for spontaneous change

$$\Delta G = \Delta H – T\Delta S < 0 \tag{19.6.4}$$

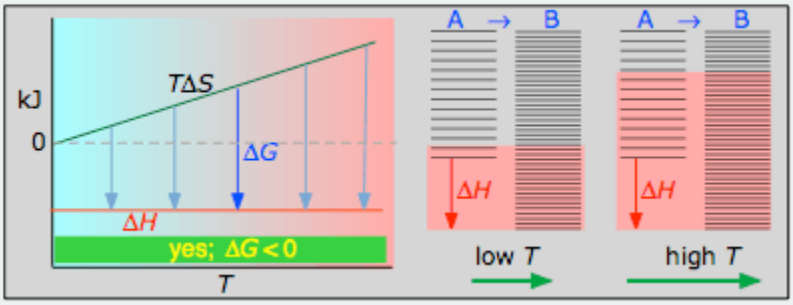
it is apparent that the temperature dependence of ΔG depends almost entirely on the entropy change associated with the process. (We say "almost" because the values of ΔH and ΔS are themselves slightly temperature dependent; both gradually increase with temperature). In particular, notice that in the above equation **the sign of the entropy change determines whether**

the reaction becomes more or less spontaneous as the temperature is raised. For any given reaction, the sign of ΔH can also be positive or negative. This means that there are four possibilities for the influence that temperature can have on the spontaneity of a process.

The following cases generalizes these relations for the four sign-combinations of ΔH and ΔS. (Note that use of the standard $\Delta H°$ and $\Delta S°$ values in the example reactions is not strictly correct here, and can yield misleading results when used generally.)

> 0

Under these conditions, both the ΔH and $T\Delta S$ terms will be negative, so ΔG will be negative regardless of the temperature. An exothermic reaction whose entropy increases will be spontaneous at all temperatures.



Example Reaction

$$C_{(graphite)} + O_{2(g)} \rightleftharpoons CO_{2(g)} \tag{19.6.5}$$

- $\Delta H°$ = –393 kJ
- $\Delta S°$ = +2.9 J K^{-1}
- $\Delta G°$ = –394 kJ at 298 K

The positive entropy change is due mainly to the greater mass of CO_2 molecules compared to those of O_2.

< 0

If the reaction is sufficiently exothermic it can force ΔG negative only at temperatures below which $|T\Delta S| < |\Delta H|$. This means that there is a temperature $T = \Delta H / \Delta S$ at which the reaction is at equilibrium; the reaction will only proceed spontaneously *below* this temperature. The freezing of a liquid or the condensation of a gas are the most common examples of this condition.

Answer available at the end of this section.

Example reaction:

$$3H_2 + N_2 \rightleftharpoons 2NH_{3(g)} \tag{19.6.6}$$

- $\Delta H°$ = –46.2 kJ
- $\Delta S°$ = –389 J K–1
- $\Delta G°$ = –16.4 kJ at 298 K

The decrease in moles of gas in the **Haber ammonia synthesis** drives the entropy change negative, making the reaction **spontaneous only at low temperatures**. Thus higher T, which speeds up the reaction, also reduces its extent.

> 0

This is the reverse of the previous case; the entropy increase must overcome the handicap of an endothermic process so that TΔS > ΔH. Since the effect of the temperature is to "magnify" the influence of a positive ΔS, the process will be spontaneous at temperatures above T = ΔH / ΔS. (Think of melting and boiling.)

Answer available at the end of this section.

Example reaction:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \tag{19.6.7}$$

- Δ*H*° = 55.3 kJ
- Δ*S*° = +176 J K^{-1}
- Δ*G*° = +2.8 kJ at 298 K

Dissociation reactions are typically endothermic with positive entropy change, and are therefore **spontaneous at high temperatures**.Ultimately, all molecules decompose to their atoms at sufficiently high temperatures.

< 0

With both Δ*H and* ΔS working against it, this kind of process will not proceed spontaneously at any temperature. Substance A always has a greater number of accessible energy states, and is therefore always the preferred form.

Answer available at the end of this section.

Example reaction:

$$½N_2 + O_2 \rightleftharpoons NO_{2(g)} \tag{19.6.8}$$

- Δ*H*° = 33.2 kJ
- Δ*S*° = –249 J $K^{-}1$
- Δ*G*° = +51.3 kJ at 298 K

This reaction is **not spontaneous at any temperature**, meaning that *its reverse is always spontaneous*. But because the reverse reaction is kinetically inhibited, NO_2 can exist indefinitely at ordinary temperatures even though it is thermodynamically unstable.

The above cases and associated plots are the important ones; do not try to memorize them, but make sure you understand and can explain or reproduce them for a given set of Δ*H* and Δ*S*.

- Their most important differentiating features are the position of the Δ*H* line (above or below the is *T*ΔS line), and the slope of the latter, which of course depends on the sign of ΔS.
- The reaction A → B will occur spontaneously only when Δ*G* is negative (blue arrows pointing down.)
- Owing to the slight temperature dependence of Δ*S,* the *T*Δ*S* plots are not quite straight lines as shown here. Similarly, the lines representing Δ*H* are even more curved.

The other two plots on each diagram are only for the chemistry-committed.

- Each pair of energy-level diagrams depicts the relative spacing of the microscopic energy levels in the reactants and products as reflected by the value of ΔS°. (The greater the entropy, the more closely-spaced are the quantized microstates.)
- The red shading indicates the range of energy levels that are accessible to the system at each temperature. The spontaneous direction of the reaction will always be in the direction in which the red shading overlaps the greater number of energy levels, resulting in the maximum dispersal of thermal energy.
- Note that the vertical offsets correspond to Δ*H*° for the reaction.
- Never forget that it is the ability of thermal energy to spread into as many of these states as possible that determines the tendency of the process to take place. None of this is to scale, of course!

Liquid-Vapor Equilibrium

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, 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,

$$\Delta G_{100^\circ\text{C}} = \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} = 40{,}657 \text{ J} - [(373.15 \text{ K})(108.96 \text{ J/K})] = 0 \text{ J} \tag{19.6.9}$$

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

$$\Delta G_{110^\circ\text{C}} = \Delta H - T\Delta S = 40{,}657 \text{ J} - [(383.15 \text{ K})(108.96 \text{ J/K})] = -1091 \text{ J} \tag{19.6.10}$$

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:

$$\Delta G_{90^\circ\text{C}} = \Delta H - T\Delta S = 40{,}657 \text{ J} - [(363.15 \text{ K})(108.96 \text{ J/K})] = 1088 \text{ J} \tag{19.6.11}$$

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 J = $-\Delta G_{90^\circ\text{C}}$, as we would predict.

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 19.6.4), 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.

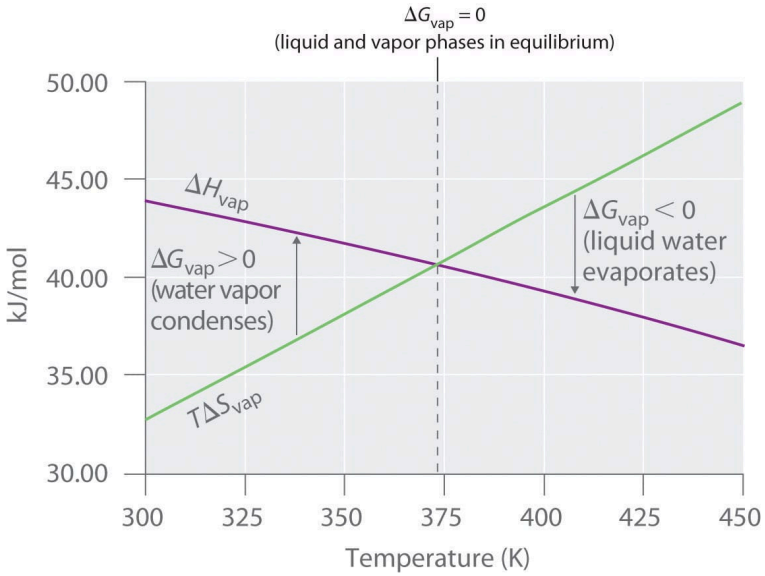


Figure 19.6.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH – TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases 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.

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.

Free Energy and the Equilibrium Constant

Δ*G* is key in determining whether or not a reaction will take place in a given direction. It turns out, however, that it is almost never necessary to explicitly evaluate Δ*G*. It is far more convenient to work with the equilibrium constant of a reaction, within which Δ*G* is "hidden". This is just as well, because for most reactions (those that take place in solutions or gas mixtures) the value of Δ*G* depends on the *proportions* of the various reaction components in the mixture; it is not a simple sum of the "products minus reactants" type, as is the case with Δ*H*.

Because ΔH° and ΔS° determine the magnitude of ΔG° and 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° and vice versa. 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 follow (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{19.6.12}$$

If a reaction is carried out at constant temperature (ΔT = 0), then Equation 19.6.12 simplifies to

$$\Delta G = V\Delta P \tag{19.6.13}$$

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 19.6.13 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):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P = nRT\frac{\Delta P}{P} = nRT\ln\left(\frac{P_\mathrm{f}}{P_\mathrm{i}}\right) \tag{19.6.14}$$

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:

$$G - G^\circ = nRT \ln P \tag{19.6.15}$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \tag{19.6.16}$$

As you will soon discover, Equation 19.6.16 allows us to relate ΔG° 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:

$$aA + bB \rightleftharpoons cC + dD \tag{19.6.17}$$

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:

$$\delta G = \sum_m G_{products} - \sum_n G_{reactants} = (cG_C + dG_D) - (aG_A + bG_B) \tag{19.6.18}$$

Substituting Equation 19.6.16 for each term into Equation 19.6.18,

$$\Delta G = [(cG^o_C + cRT \ln P_C) + (dG^o_D + dRT \ln P_D)] - [(aG^o_A + aRT \ln P_A) + (bG^o_B + bRT \ln P_B)] \tag{19.6.19}$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P^c_{\mathrm{C}} P^d_{\mathrm{D}}}{P^a_{\mathrm{A}} P^b_{\mathrm{B}}} \right) = \Delta G^\circ + RT \ln Q \tag{19.6.20}$$

where ΔG° 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, ΔG = 0 for a system at equilibrium. Therefore, we can describe the relationship between ΔG° and K_p for gases as follows:

$$0 = \Delta G^\circ + RT \ln K_p \tag{19.6.21}$$

$$\Delta G^\circ = -RT \ln K_p \tag{19.6.22}$$

If the products and reactants are in their standard states and ΔG° < 0, then K_p > 1, and products are favored over reactants. Conversely, if ΔG° > 0, then K_p < 1, and reactants are favored over products. If ΔG° = 0, then $K_p = 1$, and neither reactants nor products are favored: the system is at equilibrium.

Note

For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.

Example 19.6.1

We previosuly calculated that ΔG° = −32.7 kJ/mol of N_2 for the reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

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:

- $P_{\mathrm{N_2}}$ = 2.00 atm,

- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm,
- and T = 100°C.

Does the reaction favor products or reactants?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether products or reactants are favored

Strategy:

A. Using the values given and Equation 19.6.20, calculate Q.
B. Substitute the values of ΔG° and Q into Equation 19.6.20 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG° and ΔG under nonstandard conditions is given in Equation 19.6.20. Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Substituting the values of ΔG° and Q into Equation 19.6.20,

$$\begin{aligned}\Delta G = \Delta G^\circ + RT\ln Q &= -32.7\text{ kJ} + \left[(8.314\text{ J/K})(373\text{ K})\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)\ln(6.4\times10^{-7})\right] \\ &= -32.7\text{ kJ} + (-44\text{ kJ}) \\ &= -77\text{ kJ/mol of } N_2\end{aligned}$$

Because ΔG < 0 and Q < 1.0, the reaction is spontaneous to the right as written, so products are favored over reactants.

Exercise 19.6.1

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 × 10^{-4} atm. The value of ΔG° for this reaction is –72.5 kJ/mol of O_2. Are products or reactants favored?

Answer: –92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written, so products are favored.

Example 19.6.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. As calculated in Example 10, ΔG° for this reaction is –32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 10, ΔG°, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG° and T (in kelvins) into Equation ??? to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 10, we used tabulated values of ΔG°_f to calculate ΔG° for this reaction (–32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 19.6.22,

$$\Delta G^\circ = -RT \ln K_\text{p}$$
$$\frac{-\Delta G^\circ}{RT} = \ln K_\text{p}$$

Inserting the value of ΔG° and the temperature (25°C = 298 K) into this equation,

$$\ln K_\text{p} = -\frac{(-32.7 \text{ kJ})(1000 \text{ J/kJ})}{(8.314 \text{ J/K})(298 \text{ K})} = 13.2$$
$$K_\text{p} = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

Exercise 19.6.2

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. As calculated in the exercise in Example 10, ΔG° for this reaction is –70.5 kJ/mol of O_2.

Answer: 2.2×10^{12}

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. We described the relationship between the numerical magnitude of K_p and K in Chapter 15 and showed that they are related:

$$K_p = K(RT)^{\Delta n} \tag{19.6.23}$$

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, Δn = 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 19.6.22 can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \tag{19.6.24}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 19.6.24 for the difference between K_p and K. 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 Equations 19.6.24 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG° influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K \tag{19.6.25}$$

Equation 19.6.25 is quite powerful and connected the nature of the system under equilibrium K to the condition of the system under standard conditions ΔG^o.; that is quite powerful. Notice that K becomes larger as ΔS° 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° 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.

Note

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.

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (Figure 19.6.2). If a system is present with reactants and products present in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

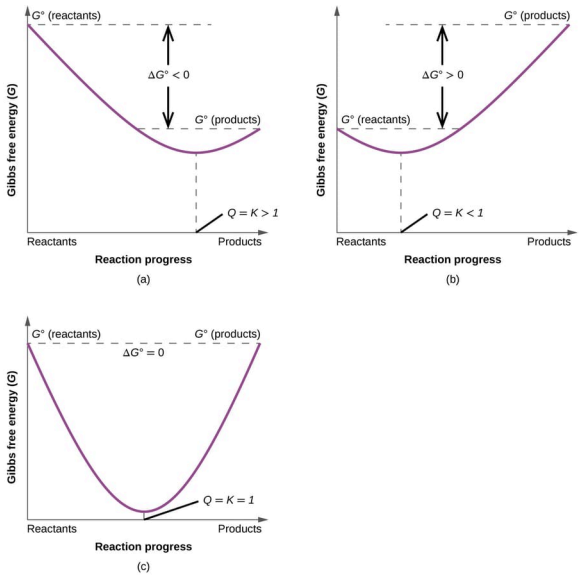


Figure 19.6.2: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

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

Relating Grxn and Kp: https://youtu.be/T-OYNTYN__4

ΔG° and ΔG: Predicting the Direction of Chemical 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 19.6.26:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{19.6.26}$$

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.

Note

A positive ΔG° means that the equilibrium constant is less than 1.

Example 19.6.3

Calculate the standard free-energy change (ΔG°) 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 19.6.26, 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:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\ \mathrm{mol\ H_2O_2} \times 109.6\ \mathrm{J/(mol \cdot K)}] \\ &\quad - \{[1\ \mathrm{mol\ H_2} \times 130.7\ \mathrm{J/(mol \cdot K)}] + [1\ \mathrm{mol\ O_2} \times 205.2\ \mathrm{J/(mol \cdot K)}]\} \\ &= -226.3\ \mathrm{J/K\ (per\ mole\ of\ H_2O_2)}\end{aligned} \tag{19.6.27}$$

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 19.6.26,

$$\begin{aligned}\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ &= -187.78\ \mathrm{kJ/mol} - (298.15\ \mathrm{K})[-226.3\ \mathrm{J/(mol \cdot K)} \times 1\ \mathrm{kJ/1000\ J}] \\ &= -187.78\ \mathrm{kJ/mol} + 67.47\ \mathrm{kJ/mol} = -120.31\ \mathrm{kJ/mol}\end{aligned}$$

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 19.6.3

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:

Video Solution

149.5 kJ/mol; no

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:

$$\Delta_f^o = \Delta H_f^o - T\Delta S_f^o \tag{19.6.28}$$

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:

$$\Delta G_{rxn}^o = \sum m\Delta G_f^o(products) - \sum n\Delta_f^o(reactants) \tag{19.6.29}$$

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.

Example 19.6.4

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). 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 ΔG°_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, ΔG°_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 19.6.4

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:

- 92.8 kJ; no

Video Solution

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.

Note

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 19.6.5

Calculate (a) ΔG° and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)\diamondsuit 2NH_3(g)$, 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
- ΔH°_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 19.6.26 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation ??? to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 19.6.26, 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:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)] \\ &= [2\text{ mol NH}_3 \times 192.8\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol N}_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol H}_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\} \\ &= -198.1\text{ J/K (per mole of N}_2\text{)}\end{aligned} \tag{19.6.30}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of ΔH°_f (NH_3) is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_f(\text{NH}_3) - [\Delta H^\circ_f(\text{N}_2) + 3\Delta H^\circ_f(\text{H}_2)] \\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})] \\ &= -91.8\text{ kJ(per mole of N}_2\text{)}\end{aligned}$$

B Inserting the appropriate values into Equation 19.6.26

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ - T\Delta S^\circ = (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) = -32.7\text{ kJ (per mole of N}_2\text{)}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300^\circ C}$ = H° and $\Delta S_{300^\circ C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation ???:

$$\begin{aligned}\Delta G_{300^\circ\text{C}} &= \Delta H_{300^\circ\text{C}} - (573\text{ K})(\Delta S_{300^\circ\text{C}}) = \Delta H^\circ - (573\text{ K})\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) = 21.7\text{ kJ (per mole of N}_2\text{)}\end{aligned}$$

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 19.6.5

Calculate

a. ΔG° and
b. $\Delta G_{750^\circ C}$

for the following reaction

$$2NO_{(g)} + O_{2\ (g)} \rightleftharpoons 2NO_{2\ (g)}$$

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. –72.5 kJ/mol of O_2
b. 33.8 kJ/mol of O_2

Video Solution

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 19.6.26, as illustrated in Example 19.6.4.

Example 19.6.6

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 19.6.3 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 19.6.26 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 19.6.26 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0 \tag{19.6.31}$$

$$\Delta H^\circ = T\Delta S^\circ \tag{19.6.32}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{-198.1\ \text{J/K}} = 463\ \text{K} \tag{19.6.33}$$

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 19.6.6

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: 792.6 K

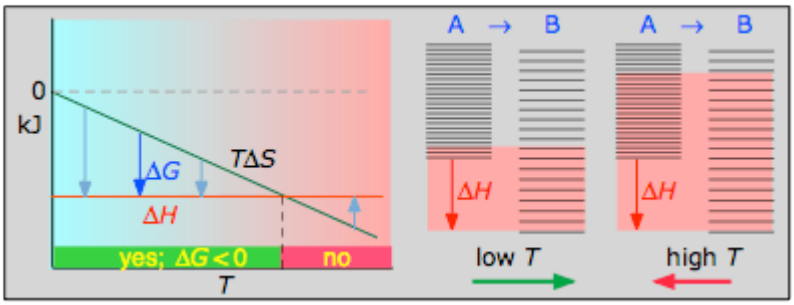
Summary

- 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.

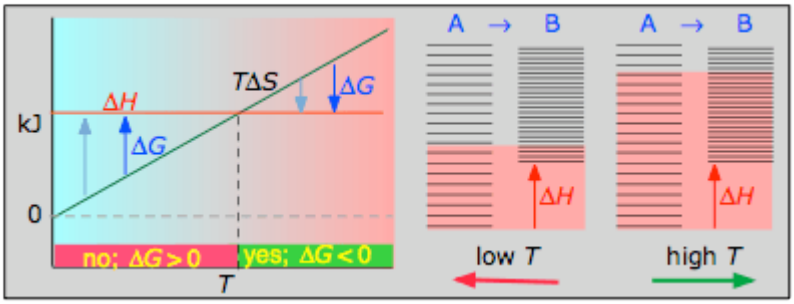
We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same 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

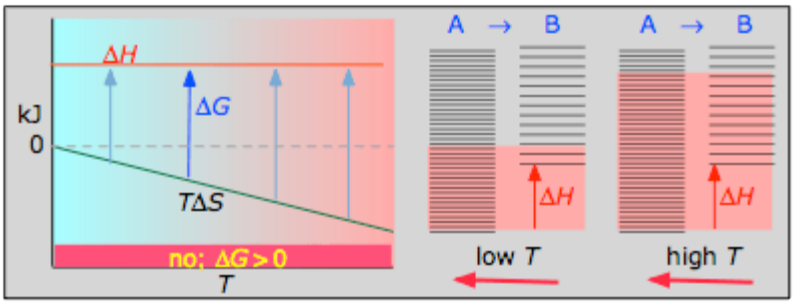
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19.7: ΔG° and K as Functions of Temperature

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

As was previously demonstrated, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G = \Delta H - T\Delta S \tag{19.7.1}$$

The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both Δ*H* and Δ*S* are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, Δ*G* will be negative if the magnitude of the *T*Δ*S* term is greater than Δ*H*. If the *T*Δ*S* term is less than Δ*H*, the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures*.
2. **Both Δ*H* and Δ*S* are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, Δ*G* will be negative if the magnitude of the *T*Δ*S* term is less than Δ*H*. If the *T*Δ*S* term's magnitude is greater than Δ*H*, the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures*.
3. **Δ*H* is positive and Δ*S* is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, Δ*G* will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures*.
4. **Δ*H* is negative and Δ*S* is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, Δ*G* will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures*.

These four scenarios are summarized in Figure 19.7.1.

Summary of the Four Scenarios for Enthalpy and Entropy Changes

	ΔH > 0 (endothermic)	**ΔH < 0 (exothermic)**
ΔS > 0 (increase in entropy)	ΔG < 0 at high temperature ΔG > 0 at low temperature Process is spontaneous at high temperature	ΔG < 0 at any temperature Process is spontaneous at any temperature
ΔS < 0 (decrease in entropy)	ΔG > 0 at any temperature Process is nonspontaneous at any temperature	ΔG < 0 at low temperature ΔG > 0 at high temperature Process is spontaneous at low temperature

Figure 19.7.1: There are four possibilities regarding the signs of enthalpy and entropy changes.

Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,\mathrm{C}(s)+\mathrm{O}_2(g) \longrightarrow 2\,\mathrm{CO}(g)$$

How does the spontaneity of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S > 0$). The reaction is therefore spontaneous ($\Delta G < 0$) at all temperatures.

Exercise 19.7.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,\mathrm{Fe}(s)+3\,\mathrm{O}_2(g) \longrightarrow 2\,\mathrm{Fe}_2\mathrm{O}_3(s)$$

How does the spontaneity of this process depend upon temperature?

Answer

ΔH and ΔS are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in “spontaneity” (as reflected by its ΔG) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG is plotted on the *y* axis versus *T* on the *x* axis:

$$\Delta G = \Delta H - T\Delta S \tag{19.7.2}$$

$$y = b + mx \tag{19.7.3}$$

Such a plot is shown in Figure 19.7.2. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the *x*-intercept of the line, that is, the value of *T* for which ΔG is zero:

$$\Delta G = 0 = \Delta H - T\Delta S \tag{19.7.4}$$

$$T = \frac{\Delta H}{\Delta S} \tag{19.7.5}$$

And so, saying a process is spontaneous at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which ΔG for the process is zero. As noted earlier, this condition describes a system at equilibrium.

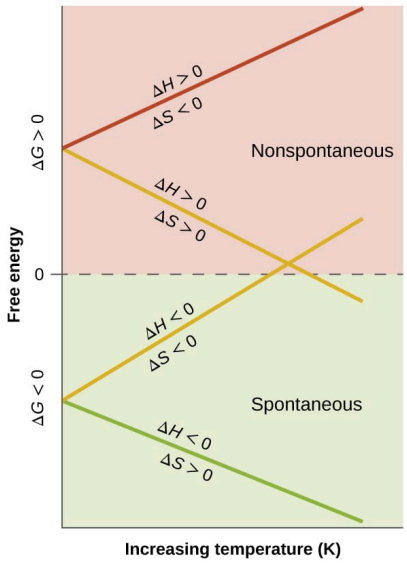


Figure 19.7.2: These plots show the variation in ΔG with temperature for the four possible combinations of arithmetic sign for ΔH and ΔS.

Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its solid and liquid phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Appendix G to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \qquad \text{or} \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from Appendix G,

$$\begin{aligned}\Delta H^\circ &= \Delta H_\mathrm{f}^\circ(\mathrm{H_2O}(g)) - \Delta H_\mathrm{f}^\circ(\mathrm{H_2O}(l)) \\ &= -241.82\ \mathrm{kJ/mol} - (-285.83\ \mathrm{kJ/mol}) = 44.01\ \mathrm{kJ/mol} \\ \Delta S^\circ &= \Delta S_{298}^\circ(\mathrm{H_2O}(g)) - \Delta S_{298}^\circ(\mathrm{H_2O}(l)) \\ &= 188.8\ \mathrm{J/K \cdot mol} - 70.0\ \mathrm{J/K \cdot mol} = 118.8\ \mathrm{J/K \cdot mol}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\ \mathrm{J/mol}}{118.8\ \mathrm{J/K \cdot mol}} = 370.5\ \mathrm{K} = 97.3\ ^\circ\mathrm{C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Appendix G). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

Exercise 19.7.4

Use the information in Appendix G to estimate the boiling point of CS_2.

Answer

313 K (accepted value 319 K)

Temperature Dependence of the Equilibrium Constant

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship can be expressed as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{19.7.6}$$

Assuming ΔH° and ΔS° are **temperature independent,** for an exothermic reaction (ΔH° < 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 19.7.6 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 19.7.6 also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° 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° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS°. 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 19.7.6 gives the following relationship at each temperature:

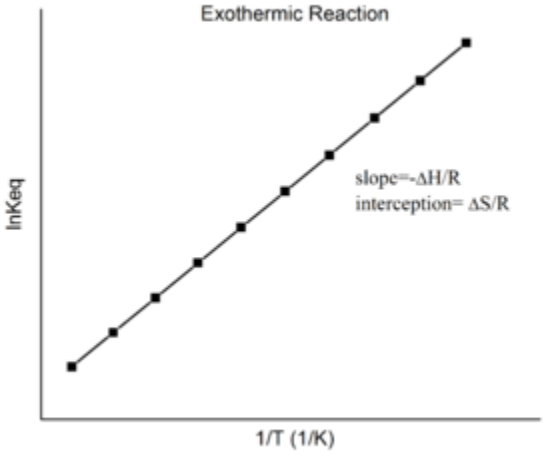
$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \tag{19.7.7}$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \tag{19.7.8}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{19.7.9}$$

Thus calculating ΔH° 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° and ΔS° are independent of temperature. The linear relation between $\ln K$and the standard enthalpies and entropies in Equation 19.7.9 is known as the van't Hoff equation. It shows that a plot of $\ln K$ vs. $1/T$ should be a line with slope $-\Delta_r H^o/R$ and intercept $\Delta_r S^o/R$.



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Hence, these thermodynamic enthalpy and entropy changes for a reversible reaction can be determined from plotting $\ln K$ vs. $1/T$ data without the aid of calorimetry. Of course, the main assumption here is that $\Delta_r H^o$ and $\Delta_r S^o$ are only very weakly dependent on T, which is usually valid over a narrow temperature range.

Example 19.7.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C is $K_p = 5.4 \times 10^5$. What is K_p at 500°C? (Use the data from Example 10.)

Given: balanced chemical equation, ΔH°, 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 kelvins. Then substitute appropriate values into Equation 19.7.9 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH° 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 19.7.9 we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{19.7.10}$$

$$= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{8.314\ \text{J/K}}\left(\frac{1}{298\ \text{K}} - \frac{1}{773\ \text{K}}\right) = -22.8 \tag{19.7.11}$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10} \tag{19.7.12}$$

$$K_2 = (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5} \tag{19.7.13}$$

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 values in the exercise in Example 10 to calculate K_p for this reaction at 1000°C.

Answer: 5.6×10^{-4}

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 Van't Hoff Equation: https://youtu.be/4vk6idAXp_A

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 $\Delta G° < 0$, then K or $K_p > 1$, and products are favored over reactants. If $\Delta G° > 0$, then K or $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, then K or $K_p = 1$, and the system is at equilibrium. We can use the measured equilibrium constant K at one temperature and $\Delta H°$ to estimate the equilibrium constant for a reaction at any other temperature.

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19.8: Coupled Reactions

Learning Objectives

Endergonic reactions can also be pushed by coupling them to another reaction, which is strongly exergonic, often through shared intermediates.

Many chemicals' reactions are *endergonic* (i.e., not spontaneous ($\Delta G > 0$)) and require energy to be externally applied to occur. However, these reaction can be *coupled* to a separate, *exergonic* (thermodynamically favorable $\Delta G < 0$) reactions that 'drive' the thermodynamically unfavorable one by coupling or 'mechanistically joining' the two reactions often via a share intermediate. Since Gibbs Energy is a state function, the ΔG values for each half-reaction may be summed, to yield the combined ΔG of the coupled reaction.

One simple example of the coupling of reaction is the decomposition of calcium carbonate:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \qquad \Delta G^o = 130.40\ kJ/mol \tag{19.8.1}$$

The strongly positive ΔG for this reaction is reactant-favored. If the temperature is raised above 837 °C, this reaction becomes spontaneous and favors the products. Now, let's consider a second and completely different reaction that can be coupled ot this reaction. The combustion of coal released by burning the coal $\Delta G^o = -394.36\ \ kJ/mol$ is greater than the energy required to decompose calcium carbonate ($\Delta G^o = 130.40\ \ kJ/mo$).

$$C_{(s)} + O_2 \rightleftharpoons CO_{2(g)} \qquad \Delta G^o = -394.36\ kJ/mol \tag{19.8.2}$$

If reactions 19.8.1 and 19.8.2 were added

$$CaCO_{3(s)} + C_{(s)} + O_2 \rightleftharpoons CaO_{(s)} + 2CO_[2(g) \quad \Delta G^o = -263.96\ kJ/mol \tag{19.8.3}$$

and then Hess's Law were applied, the combined reaction (Equation 19.8.3) is product-favored with $\Delta G^o = -263.96\ \ kJ/mol$. This is because the reactant-favored reaction (Equation 19.8.2) is linked to a strong spontaneous reaction so that both reactions yield products. Notice that the ΔG for the coupled reaction is the sum of the constituent reactions; this is a consequence of Gibbs energy being a state function:

$$\Delta G^o = 130.40\ kJ/mol + -394.36\ kJ/mol = -263.96\ kJ/mol \tag{19.8.4}$$

Coupled Reactions in Biology

This is a common feature in biological systems where some enzyme-catalyzed reactions are interpretable as two coupled half-reactions, one spontaneous and the other non-spontaneous. Organisms often the hydrolysis of **ATP** (adenosine triphosphate) to generate **ADP** (adenosine diphosphate) as the spontaneous coupling reaction (Figure 19.8.1).

$$ATP + H_2O \rightleftharpoons ADP + P_i \tag{19.8.5}$$

- P_i is inorganic phosphate ion

The phosphoanhydride bonds formed by ejecting water between two phosphate group of ATP exhibit a large negative $-\Delta G$ of hydrolysis and are thus often termed "high energy" bonds. However, as with all bonds, energy is requires to break these bonds, but the thermodynamic Gibbs energy difference is strongly "energy releasing" when including the solvation thermodynamics of the phosphate ions; ΔG for this reaction is - 31 kJ/mol.

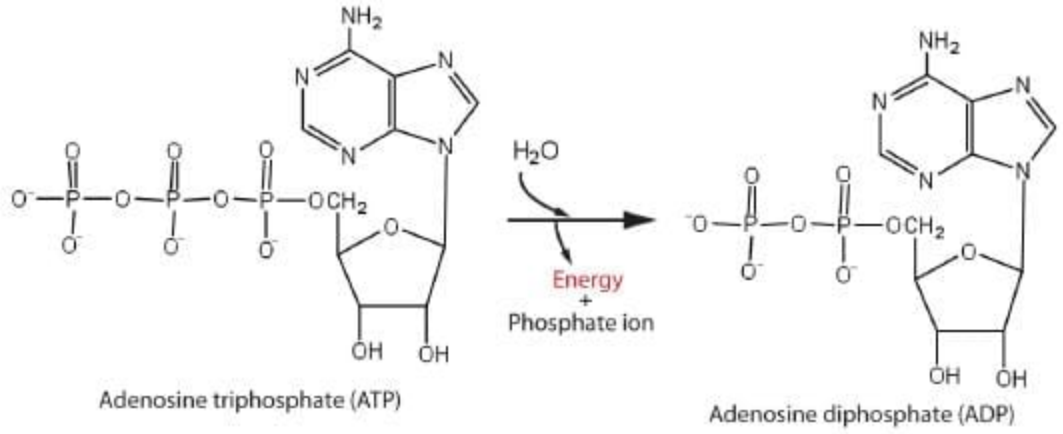


Figure 19.8.1: *Hydrolysis of ATP to Form ADP*

ATP is the major 'energy' molecule produced by metabolism, and it serves as a sort of 'energy source' in cell: ATP is dispatched to wherever a non-spontaneous reaction needs to occurs so that the two reactions are coupled so that the overall reaction is thermodynamically favored.

Example 19.8.1: Phosphorylating Carboxylic Acids

Aldehydes $RCHO$ are organic compounds that can be oxidized to generate carboxylic acids and nicotinamide adenine dinucleotide (NAD) is a coenzyme found in all living cells and in the reduced form, NAD^+, it acts as an oxidizing agent that can accept electrons from other molecules.

The NAD$^+$-linked oxidation of an aldehyde is practically irreversible with an equilibrium that strongly favors the products ($\Delta G >> 0$:

$$RCHO + NAD^+ + H_2O \rightleftharpoons RCOOH + NADH + H^+ \tag{19.8.6}$$

The position of equilibrium for phosphorylating carboxylic acids lies very much to the left:

$$RCOOH + P_i \rightleftharpoons RC(=O)(O-P_i) + H_2O \tag{19.8.7}$$

- (P_i\) is inorganic phosphate ion.

The non-spontaneous formation of a phosphorylated carboxylic acid can be driven by coupling it to the (spontaneous) NAD$^+$-linked oxidation of an aldehyde?

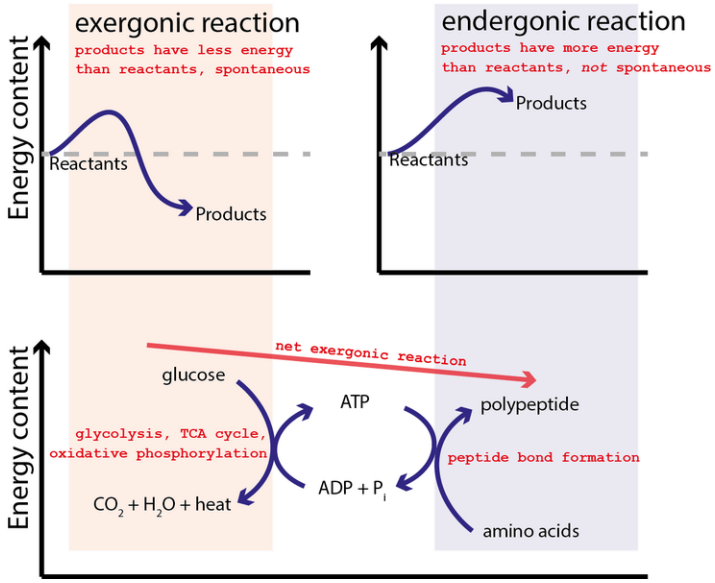


Figure 19.8.2: A reaction will not proceed spontaneously unless the products of the reaction have lower energy than the reactants. This is called an exergonic reactions. A reaction where the products have higher energy than the reactions (energonic reaction) can only proceed when there is an input of energy. Exergonic reactions like burning of glucose drives ATP synthesis. The ATP molecules are used to power other endergonic reactions like protein synthesis. from Wikipedia (Muessig).

Similarly, ATP hydrolysis can be used to combine amino acids together to generate polypeptides (and proteins) as graphically illustrated by Figure 19.8.2. In this case, the reverse of Equation 19.8.5 is initially coupled to the oxidizing glucose by oxygen

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \tag{19.8.8}$$

Reaction 19.8.8 is strongly spontaneous with $\Delta G = -2880\ \ kJ/mol$ or close to 100x greater energy capability than the hydrolysis of ATP in Equation 19.8.5. Hence, the equilibrium for this reaction so strongly favors the products that a single arrow is typically used in the chemical equation as it is essential irreversible. It may not be surpising that glucose and all sugars are very energetic moleculess since they are the primary energy source for life.

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Summary

Two (or more) reactions may be combined such that a spontaneous reaction may be made 'drive' an nonspontaneous one. Such reactions may be considered *coupled*. Changes in Gibbs energy of the coupled reactions are additive.

Contributors and Attributions

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19.E: Chemical Thermodynamics (Exercises)

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20: ELECTROCHEMISTRY

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

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20.1: Electrode Potentials and their Measurement

Learning Objectives

- To distinguish between galvanic and electrolytic cells.

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:

$$Zn_{(s)} + Br_{2(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Br^{-}_{(aq)} \tag{20.1.1}$$

The half-reactions are as follows:

reduction half-reaction:

$$Br_{2(aq)} + 2e^{-} \rightarrow 2Br^{-}_{(aq)} \tag{20.1.2}$$

oxidation half-reaction:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-} \tag{20.1.3}$$

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 Br_2 is the oxidant (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 20.1.1). 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.

Note

In any redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

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 20.1.1). 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 20.1.1: 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.

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Electrochemical Cells: https://youtu.be/nyS1BQ2ZVIg

Galvanic (Voltaic) 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:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{20.1.4}$$

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 20.1.2: 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 Zn^{2+}(aq) ions, while 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.

This same reaction can be carried out using the galvanic cell illustrated in part (a) in Figure 20.1.3. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of Cu^{2+} ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of 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 Na^+ or K^+ and NO_3^- or 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 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 Zn^{2+} solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the Cu^{2+} solution decreases (part (b) in Figure 20.1.3). 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 20.1.2: 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.

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 galvanic cell. *This galvanic cell illustrates the use of a salt bridge to connect two solutions.*

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 (part (a) in Figure 20.1.3). 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.

Note

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.

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 20.1.1.

Example 20.1.1

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:

$$3Sn_{(s)} + 2NO^{-}_{3(aq)} + 8H^{+}_{(aq)} \rightarrow 3Sn^{2+}_{(aq)} + 2NO_{(g)} + 4H_2O_{(l)} \tag{20.1.5}$$

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. **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:

$$\text{reduction: } NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$$

$$\text{oxidation: } Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

b. 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.
c. **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 20.1.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of MnO_4^- in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of 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:

$$2MnO^{-}_{4(aq)} + 5Sn^{2+}_{(aq)} + 16H^{+}_{(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 5Sn^{4+}_{(aq)} + 8H_2O_{(l)} \tag{20.1.6}$$

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. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$; $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$
b. The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.
c. 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.

Constructing Cell Diagrams

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 part (a) in Figure $20.1.3$ is written as follows:

Figure $20.1.3$.

A cell diagram includes solution concentrations when they are provided.

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:

$$Pt_{(s)} \,|\, H_{2(g)} | HCl_{(aq)} \,|\, AgCl_{(s)}\, Ag_{(s)} \tag{20.1.7}$$

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:

$$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)} \tag{20.1.8}$$

anode reaction:

$$\frac{1}{2}\,\mathrm{H_{2(g)}} \rightarrow \mathrm{H^+_{(aq)}} + \mathrm{e^-} \tag{20.1.9}$$

overall:

$$\mathrm{AgCl_{(s)}} + \frac{1}{2}\mathrm{H_{2(g)}} \rightarrow \mathrm{Ag_{(s)}} + \mathrm{Cl^-_{(aq)}} + \mathrm{H^+_{(aq)}} \tag{20.1.10}$$

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 $20.1.2$

Draw a cell diagram for the galvanic cell described in Example 1. The balanced chemical reaction is as follows:

$$3Sn_{(s)} + 2NO^-_{3(aq)} + 8H^+_{(aq)} \rightarrow 3Sn^{2+}_{(aq)} + 2NO_{(g)} + 4H_2O_{(l)} \tag{20.1.11}$$

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 Sn(s)|Sn^{2+}(aq). We could include H_2SO_4(aq) with the contents of the anode compartment, but the sulfate ion (as 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 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,

$$Sn_{(s)} \,|\, Sn^{2+}_{(aq)} \,||\, HNO_{3(aq)} \,|\, NO_{(g)} \,|\, Pt_{(s)} \tag{20.1.12}$$

The solution concentrations were not specified, so they are not included in this cell diagram.

Exercise 20.1.2

Draw the cell diagram for the following reaction, assuming the concentration of Ag^+ and Mg^{2+} are each 1 M:

$$Mg_{(s)} + 2Ag^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + 2Ag_{(s)} \tag{20.1.13}$$

Answer

$$Mg(s) \,|\, Mg^{2+}(aq, 1M \,||\, Ag^+(aq, 1M) \,|\, Ag(s) \tag{20.1.14}$$

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Cell Diagrams: https://youtu.be/IKqOAfivem8

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.

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20.2: Standard Electrode Potentials

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.

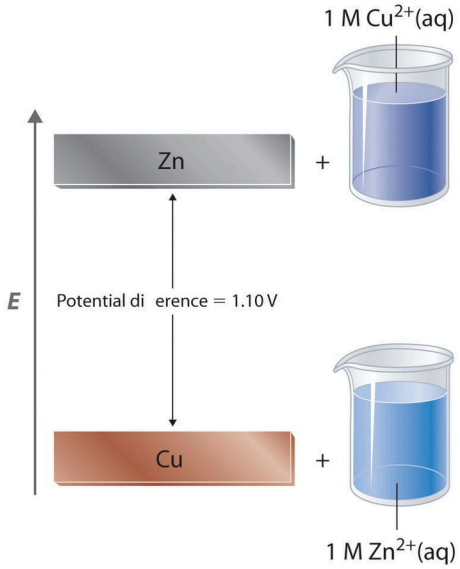


Figure 20.2.1: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic Zn and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous Zn^{2+} ions. Much of this potential energy difference is because 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 19.3 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 nonideal 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.

> **Note**
>
> 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:

$$Co_{(s)} \mid Co^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E°= 0.59\ V \tag{20.2.1}$$

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:

$$E°_{cell} = E°_{cathode} - E°_{anode} \tag{20.2.2}$$

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 20.2.2, 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.

> **Note**
>
> The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials:
>
> $$E°_{cell} = E°_{cathode} - E°_{anode} \tag{20.2.3}$$

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 20.2.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{20.2.4}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

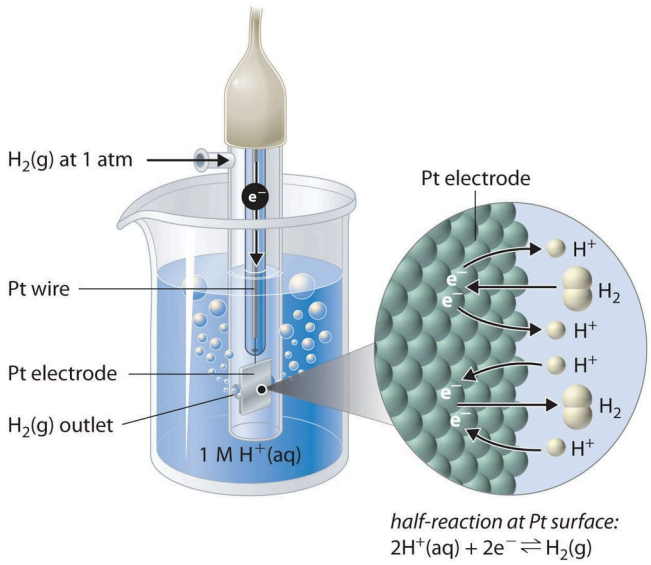


Figure 20.2.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules 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.

Figure 20.2.3 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:

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel H^+(aq, 1M) \mid H_2(g, 1atm) \mid Pt_{(s)} \tag{20.2.5}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E°_{cathode} = 0V \tag{20.2.6}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E°_{anode} = -0.76\ V \tag{20.2.7}$$

- overall:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{20.2.8}$$

$$E°_{cell} = E°_{cathode} - E°_{anode} = 0.76\ V \tag{20.2.9}$$

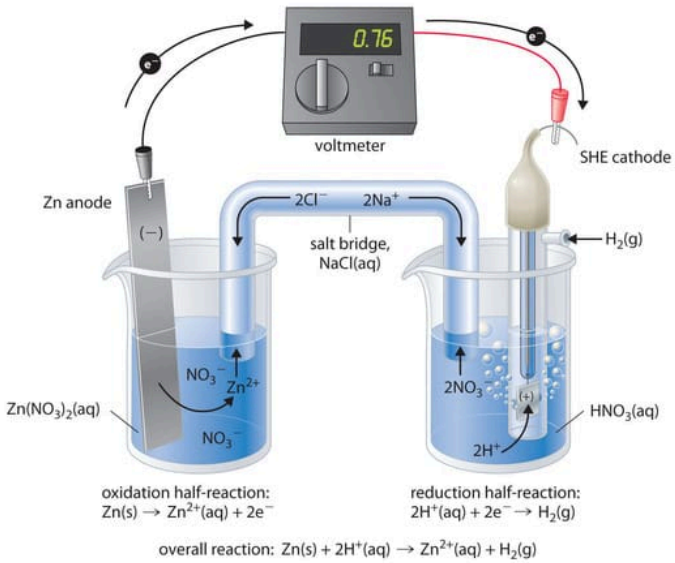


Figure 20.2.3: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to 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.

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 − (−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.

Note

E° values do **NOT** depend on the stoichiometric coefficients for a half-reaction, because it is an *intensive* property.

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 20.2.3 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:

$$Pt_{(s)} \mid H_2(g, 1atm) \mid H^+(aq, 1\ M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{20.2.10}$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu_{(g)} \quad E°_{cathode} = 0.34\ V \tag{20.2.11}$$

- Anode:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \quad E°_{anode} = 0\ V \tag{20.2.12}$$

- Overall:

$$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)} \tag{20.2.13}$$

$$E°_{cell} = E°_{cathode} - E°_{anode} = 0.34\ V \tag{20.2.14}$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

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Electrode Potentials and ECell: https://youtu.be/zeeAXleT1c0

Balancing Redox Reactions Using the Half-Reaction Method

Previously, 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:

$$Al_{(s)} + OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + H_{2(g)} \tag{20.2.15}$$

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:

$$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)} \tag{20.2.16}$$

- oxidation:

$$Al_{(s)} + 4OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + 3e^- \tag{20.2.17}$$

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 20.2.16, two H^+ ions gain one electron each in the reduction; in Equation 20.2.17, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 20.2.16) by 3 and the oxidation half-reaction (Equation 20.2.17) by 2 to give the same number of electrons in both half-reactions:

- Adding the two half-reactions,

$$6H_2O_{(l)} + 2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-4(aq) + 3H_{2(g)} + 6OH^-_{(aq)} \tag{20.2.18}$$

Simplifying by canceling substances that appear on both sides of the equation,

$$6H_2O_{(l)} + 2Al_{(s)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{20.2.19}$$

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:

$$2Al + 8O + 14H = 2Al + 8O + 14H \tag{20.2.20}$$

The atoms also balance, so Equation 20.2.19 is a balanced chemical equation for the redox reaction depicted in Equation 20.2.15.

Note

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 20.2.15, hydrogen is reduced from H^+ in OH^- to H_2, and aluminum is oxidized from Al° to Al^{3+}:

- **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:

  - Balancing H atoms by adding H^+, we obtain the following:
    - 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+}:

      - **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 ??? (the reductive half-reaction) by 3 and Equation ??? (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

        - **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 $6e^-$,

$$2Al_{(s)} + 5H_2O_{(l)} + 3OH^-_{(aq)} + H^+_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{20.2.21}$$

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:

$$2Al_{(s)} + 6H_2O_{(l)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{20.2.22}$$

Step 6: Check to make sure that all atoms and charges are balanced.

Equation 20.2.22 is identical to Equation 20.2.19, obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

Example 20.2.1

In acidic solution, the redox reaction of dichromate ion ($Cr_2O^{2-}_7$) 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 20.2.4):

$$Cr_2O^{2-}_{7(aq)} + I^-_{(aq)} \rightarrow Cr^{3+}_{(aq)} + I_{2(aq)} \tag{20.2.23}$$

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:

$$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}(_{(aq)} + 7H_2O_{(l)} \tag{20.2.24}$$

- oxidation:

$$2I^-_{(aq)} \rightarrow I_{2(aq)} + 2e^- \tag{20.2.25}$$

Balancing the number of electrons by multiplying the oxidation reaction by 3,

- oxidation:

$$6I^-_{(aq)} \rightarrow 3I_{2(aq)} + 6e^- \tag{20.2.26}$$

Adding the two half-reactions and canceling electrons,

$$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6I^-_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 3I_{2(aq)} \tag{20.2.27}$$

We must now check to make sure the charges and atoms on each side of the equation balance:

$$(-2) + 14 + (-6) = +6$$
$$+6 = +6$$

2Cr + 7O+ 14H+ 6I = 2Cr + 7O + 14H + 6I

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 $Cr_2O_7^{2-}$ to Cr^{3+}, and I^- ions are oxidized to I_2. Dividing the reaction into two half-reactions,

- reduction:

$$Cr_2O_{7(aq)}^{2-} \rightarrow Cr_{(aq)}^{3+} \tag{20.2.28}$$

- oxidation:

$$I_{(aq)}^{-} \rightarrow I_{2(aq)} \tag{20.2.29}$$

Step 2: Balancing the atoms other than oxygen and hydrogen,

- reduction:

$$Cr_2O_{7(aq)}^{2-} \rightarrow 2Cr_{(aq)}^{3+} \tag{20.2.30}$$

- oxidation:

$$2I_{(aq)}^{-} \rightarrow I_{2(aq)} \tag{20.2.31}$$

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:

$$Cr_2O_{7(aq)}^{2-} \rightarrow 2Cr_{(aq)}^{3+} + 7H_2O_{(l)} \tag{20.2.32}$$

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:

$$Cr_2O_{7(aq)}^{2-} + 14H_{(aq)}^{+} \rightarrow 2Cr_{(aq)}^{3+} + 7H_2O_{(l)} \tag{20.2.33}$$

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,

- $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$

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 20.2.1

Copper is found as the mineral covellite (CuS). The first step in extracting the copper is to dissolve the mineral in nitric acid (HNO_3), which oxidizes sulfide to sulfate and reduces nitric acid to NO:

$$CuS_{(s)} + HNO_{3(aq)} \rightarrow NO_{(g)} + CuSO_{4(aq)} \tag{20.2.34}$$

Balance this equation using the half-reaction method.



Figure by Didier Descouens. Image used by permission of Wikipedia

Answer

$$3CuS_{(s)} + 8HNO3(aq) \rightarrow 8NO_{(g)} + 3CuSO_{4(aq)} + 4H_2O_{(l)} \tag{20.2.35}$$

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Balancing a Redox Reaction in Acidic Conditions: https://youtu.be/IB-fWLsI0lc

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:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{20.2.36}$$

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 $E°_{cell}$:

$$E°_{cell} = E°_{cathode} - E°_{anode} = 1.10\ V \tag{20.2.37}$$

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, 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 4 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

Note

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 20.2.2

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:

$$\text{cathode: } Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$

$$\text{anode: } Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$$

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 20.2.2 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 20.2.2:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$0.27\ V = E°_{cathode} - (-0.55\ V)$$

$$E°_{cathode} = -0.28\ V$$

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 $E° = -(-0.28\ V) = 0.28\ V$ 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 20.2.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $Hg(CH_3CO_2)_2$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode: $Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$
- anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the anode?

Answer 0.85 V

We can use this procedure described to measure the standard potentials for a wide variety of chemical substances, some of which are listed in Table P2. These data allow us to compare the oxidative and reductive strengths of a variety of substances. The half-reaction for the standard hydrogen electrode (SHE) lies more than halfway down the list in Table 20.2.1. All reactants that lie below the SHE in the table are stronger oxidants than H^+, and all those that lie above the SHE are weaker. The strongest oxidant in the table is F_2, with a standard electrode potential of 2.87 V. This high value is consistent with the high electronegativity of fluorine and tells us that fluorine has a stronger tendency to accept electrons (it is a stronger oxidant) than any other element.

Table 20.2.1: Standard Potentials for Selected Reduction Half-Reactions at 25°C

Half-Reaction
$Li^+(aq) + e^- \rightleftharpoons Li(s)$
$Be^{2+}(aq) + 2e^- \rightleftharpoons Be(s)$
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$
$Ag_2S(s) + 2e^- \rightleftharpoons 2Ag(s) + S^{2-}(aq)$
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$
$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$
$2SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons S_2O_6^{2-}(aq) + 2H_2O(l)$
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$

Half-Reaction
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$
$H_2SO_3(aq) + 4H^+(aq) + 4e^- \rightleftharpoons S(s) + 3H_2O(l)$
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$
$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$
$H_2SeO_3(aq) + 4H^+ + 4e^- \rightleftharpoons Se(s) + 3H_2O(l)$
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$
$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons HNO_2(aq) + H_2O(l)$
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$ (20.2.38)
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$

Similarly, all species in Table 20.2.1 that lie above H_2 are stronger reductants than H_2, and those that lie below H_2 are weaker. The strongest reductant in the table is thus metallic lithium, with a standard electrode potential of –3.04 V. This fact might be surprising because cesium, not lithium, is the least electronegative element. The apparent anomaly can be explained by the fact that electrode potentials are measured in aqueous solution, where intermolecular interactions are important, whereas ionization potentials and electron affinities are measured in the gas phase. Due to its small size, the Li^+ ion is stabilized in aqueous solution by strong electrostatic interactions with the negative dipole end of water molecules. These interactions result in a significantly greater $\Delta H_{hydration}$ for Li^+ compared with Cs^+. Lithium metal is therefore the strongest reductant (most easily oxidized) of the alkali metals in aqueous solution.

Note

Species in Talbe Table 20.2.1 (or Table P2) that lie above H_2 are stronger reducing agents (more easily oxidized) than H_2. Species that lie below H_2 are stronger oxidizing agents.

Because the half-reactions shown in Table 20.2.1 are arranged in order of their E° values, we can use the table to quickly predict the relative strengths of various oxidants and reductants. Any species on the left side of a half-reaction will spontaneously oxidize any species on the right side of another half-reaction that lies below it in the table. Conversely, any species on the right side of a half-reaction will spontaneously reduce any species on the left side of another half-reaction that lies above it in the table. We can use these generalizations to predict the spontaneity of a wide variety of redox reactions ($E°_{cell} > 0$), as illustrated below.

Example 20.2.3

The black tarnish that forms on silver objects is primarily Ag_2S. The half-reaction for reversing the tarnishing process is as follows:

$$Ag_2S(s)+2e^- \rightarrow 2Ag(s)+S^{2-}(aq) \quad E°=-0.69\ V$$

a. Referring to Table 20.2.1, predict which species—$H_2O_2(aq)$, Zn(s), $I^-(aq)$, $Sn^{2+}(aq)$—can reduce Ag_2S to Ag under standard conditions.

b. Of these species—$H_2O_2(aq)$, Zn(s), $I^-(aq)$, $Sn^{2+}(aq)$, identify which is the strongest reducing agent in aqueous solution and thus the best candidate for a commercial product.

c. From the data in Table 20.2.1, suggest an alternative reducing agent that is readily available, inexpensive, and possibly more effective at removing tarnish.



Given: reduction half-reaction, standard electrode potential, and list of possible reductants

Asked for: reductants for Ag_2S, strongest reductant, and potential reducing agent for removing tarnish

Strategy:

A From their positions inTable 20.2.1, decide which species can reduce Ag_2S. Determine which species is the strongest reductant.

B Use Table 20.2.1 to identify a reductant for Ag_2S that is a common household product.

Solution

We can solve the problem in one of two ways: (1) compare the relative positions of the four possible reductants with that of the Ag_2S/Ag couple in Table 20.2.1 or (2) compare E° for each species with E° for the Ag_2S/Ag couple (−0.69 V).

a. **A** The species in Table 20.2.1 are arranged from top to bottom in order of increasing reducing strength. Of the four species given in the problem, $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$ lie above Ag_2S, and one [Zn(s)] lies below it. We can therefore conclude that Zn(s) can reduce $Ag_2S(s)$ under standard conditions, whereas $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$ cannot. $Sn^{2+}(aq)$ and $H_2O_2(aq)$ appear twice in the table: on the left side (oxidant) in one half-reaction and on the right side (reductant) in another.

b. The strongest reductant is Zn(s), the species on the right side of the half-reaction that lies closer to the bottom of Table 20.2.1 than the half-reactions involving $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$. (Commercial products that use a piece of zinc are often marketed as a "miracle product" for removing tarnish from silver. All that is required is to add warm water and salt for electrical conductivity.)

c. **B** Of the reductants that lie below Zn(s) in Table 20.2.1, and therefore are stronger reductants, only one is commonly available in household products: Al(s), which is sold as aluminum foil for wrapping foods.

Example 20.2.4

Use the data in Table 20.2.1 to determine whether each reaction is likely to occur spontaneously under standard conditions:

a. $Sn(s) + Be^{2+}(aq) \rightarrow Sn^{2+}(aq) + Be(s)$

b. $MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow O_2(g) + Mn^{2+}(aq) + 2H_2O(l)$

Given: redox reaction and list of standard electrode potentials (Table P2)

Asked for: reaction spontaneity

Strategy:

A. Identify the half-reactions in each equation. Using Table 20.2.1, determine the standard potentials for the half-reactions in the appropriate direction.

B. Use Equation 20.2.2 to calculate the standard cell potential for the overall reaction. From this value, determine whether the overall reaction is spontaneous.

Solution

a. **A** Metallic tin is oxidized to $Sn^{2+}(aq)$, and $Be^{2+}(aq)$ is reduced to elemental beryllium. We can find the standard electrode potentials for the latter (reduction) half-reaction (−1.85 V) and for the former (oxidation) half-reaction (−0.14 V) directly from Table 20.2.1.

B Adding the two half-reactions gives the overall reaction:

$\text{cathode: } Be^{2+}(aq) + 2e^- \rightarrow Be(s)$ $\text{anode: } Sn(s) \rightarrow Sn^{2+}(s) + 2e^-$ $\text{total: } Sn(s) + Be^{2+}(aq) \rightarrow Sn^{2+}(aq) + Be(s)$	$E^\circ_{\text{cathode}} = -1.99 \text{ V}\ E^\circ_{\text{anode}} = -0.14 \text{ V}\ E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -1.85 \text{ V}$

The standard cell potential is quite negative, so the reaction will not occur spontaneously as written. That is, metallic tin cannot reduce Be^{2+} to beryllium metal under standard conditions. Instead, the reverse process, the reduction of stannous ions (Sn^{2+}) by metallic beryllium, which has a positive value of $E°_{cell}$, will occur spontaneously.

b. **A** MnO_2 is the oxidant (Mn^{4+} is reduced to Mn^{2+}), while H_2O_2 is the reductant (O^{2-} is oxidized to O_2). We can obtain the standard electrode potentials for the reduction and oxidation half-reactions directly from Table 20.2.1.

B The two half-reactions and their corresponding potentials are as follows

$\begin{aligned}&\text{cathode:}\mathrm{MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)}\\&\text{anode:}\mathrm{H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-}\\&\text{overall:}\mathrm{MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow O_2(g) + Mn^{2+}(aq) + 2H_2O(l)}\end{aligned}$	$E°_{\text{cathode}} = 1.22\ \text{V}\ E°_{\text{anode}} = 0.70\ \text{V}\ E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}} \quad = -0.53\ \text{V}$

The standard potential for the reaction is positive, indicating that under standard conditions, it will occur spontaneously as written. Hydrogen peroxide will reduce MnO_2, and oxygen gas will evolve from the solution.

Exercise 20.2.4

Use the data in Table 20.2.1 to determine whether each reaction is likely to occur spontaneously under standard conditions:

1. $2Ce^{4+}(aq) + 2Cl^-(aq) \rightarrow 2Ce^{3+}(aq) + Cl_2(g)$
2. $4MnO_2(s) + 3O_2(g) + 4OH^-(aq) \rightarrow 4MnO_4^-(aq) + 2H_2O$

Answer

1. spontaneous ($E°_{cell}$ = 0.36 V)
2. nonspontaneous ($E°_{cell}$ = −0.20 V)

Although the sign of $E°_{cell}$ tells us whether a particular redox reaction will occur spontaneously under standard conditions, it does not tell us to what extent the reaction proceeds, and it does not tell us what will happen under nonstandard conditions. To answer these questions requires a more quantitative understanding of the relationship between electrochemical cell potential and chemical thermodynamics.

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.

Note

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:

$$Cl^-_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)} \tag{20.2.39}$$

$$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)} \tag{20.2.40}$$

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 20.2.4). 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:

$$Pt_{(s)} \mid Hg_2Cl_{2(s)} \mid KCl_{(aq,sat)} \tag{20.2.41}$$

$$Hg_2Cl_{2(s)} + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-(aq) \tag{20.2.42}$$

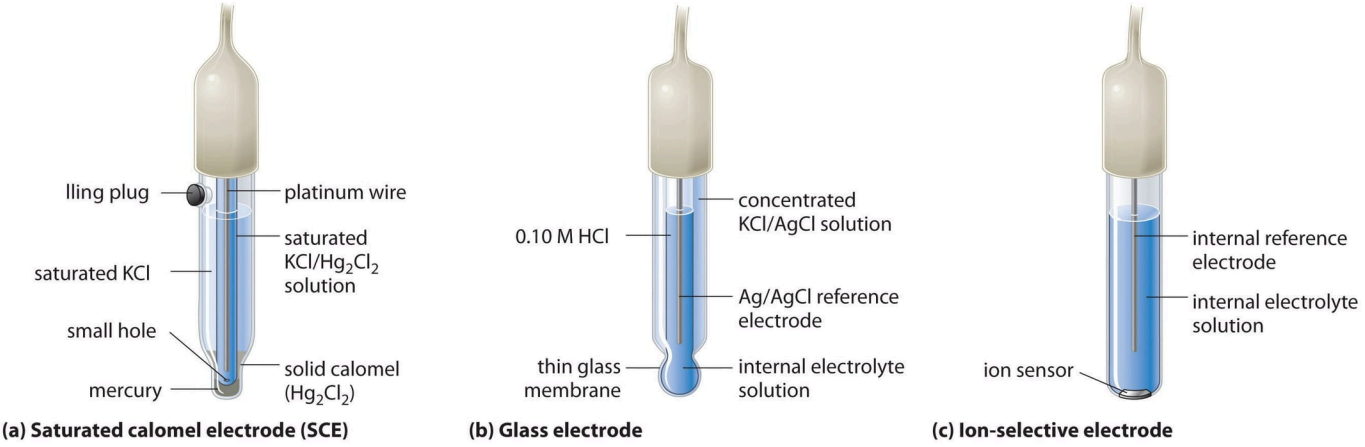


Figure 20.2.4: Three Common Types of Electrodes. (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior 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.

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 20.2.5). 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^+]:

$$E_{glass} = E' + (0.0591\ V \times \log[H^+]) = E' - 0.0591\ V \times pH \tag{20.2.43}$$

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 20.2.5). 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 20.2.2.

Table 20.2.2: 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

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 Standard Hydrogen Electrode (SHE): https://youtu.be/GS-SE7IDDtY

Summary

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.

The oxidative and reductive strengths of a variety of substances can be compared using standard electrode potentials. Apparent anomalies can be explained by the fact that electrode potentials are measured in aqueous solution, which allows for strong

intermolecular electrostatic interactions, and not in the gas phase.

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°.

Contributors and Attributions

- Anonymous

- cathode:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E°_{cathode} = 0.34\ V \tag{20.2.44}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}(aq, 1M) + 2e^- \qquad E°_{anode} = -0.76\ V \tag{20.2.45}$$

- overall:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{20.2.46}$$

- Redox reactions can be balanced using the half-reaction method.
- The standard cell potential is a measure of the driving force for the reaction.
- The relative strengths of various oxidants and reductants can be predicted using E° values.

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20.3: Ecell, ΔG, and K

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:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{20.3.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}.

Example 20.3.1

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 20.3.1 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 20.3.1. 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 20.3.1

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,

$$\Delta G^\circ = F\left[(-0.77V) + (-2)(-0.45V)\right] = F(0.13V)$$

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 20.3.1 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 20.3.1), we can write

$$-nFE^\circ_{cell} = -RT \ln K$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{20.3.2}$$

For $T = 298\ K$, Equation 20.3.2 can be simplified as follows:

$$\begin{aligned} E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right) \ln K \\ &= \left[\frac{[8.314\ \text{J/(mol} \cdot \text{K)(298 K)}]}{n[96,485\ \text{J/(V} \cdot \text{mol)}]}\right] 2.303 \log K \\ &= \left(\frac{0.0592\ \text{V}}{n}\right) \log K \end{aligned} \tag{20.3.3}$$

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 20.3.2

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 20.3.3 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 20.3.3 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).

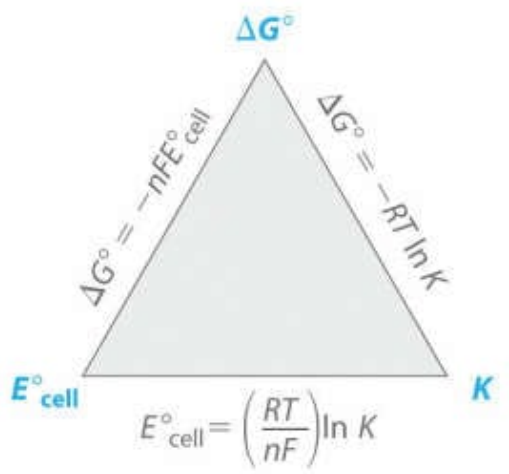
Exercise 20.3.2

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 20.3.1 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 ($\Delta G^\circ < 0$). 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 20.3.1: 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 20.3.1

−44 kJ/mol I_2; yes

Exercise 20.3.2

5.7×10^{72}

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20.4: Cell Potential as a Function of Concentrations

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:

$$\Delta G = \Delta G° + RT \ln Q \tag{20.4.1}$$

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 20.4.1, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT \ln Q \tag{20.4.2}$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q \tag{20.4.3}$$

Equation 20.4.3 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 20.4.3 reduces to Equation 20.4.4 and 20.4.5 because $Q = K$, and there is no net transfer of electrons (i.e., $E_{cell} = 0$).

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln K = 0 \tag{20.4.4}$$

since

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{20.4.5}$$

Substituting the values of the constants into Equation 20.4.3 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):

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{20.4.6}$$

The Power of the Nernst Equation

The Nernst Equation (20.4.3) 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 20.4.6 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 20.4.6 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 20.4.1

The following reaction proceeds spontaneously under standard conditions because $E°_{cell} > 0$ (which means that $\Delta G° < 0$):

$$2\,Ce^{4+}\,(aq) + 2\,Cl^{-}\,(aq) \longrightarrow 2\,Ce^{3+}\,(aq) + Cl_2\,(g) \qquad E°_{cell} = 0.25\,V$$

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 20.4.6 instead of Equation 20.4.3. 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 20.4.6,

$$\begin{aligned} E_{\text{cell}} &= E°_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0.25\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{[\text{Ce}^{3+}]^2 P_{\text{Cl}_2}}{[\text{Ce}^{4+}]^2[\text{Cl}^-]^2}\right) \\ &= 0.25\ \text{V} - [(0.0296\ \text{V})(8.37)] = 0.00\ \text{V} \end{aligned}$$

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 20.4.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4\,\text{MnO}_2\,(s) + 3\,\text{O}_2\,(g) + 4\,\text{OH}^-\,(aq) \longrightarrow 4\,\text{MnO}_4^-\,(aq) + 2\,\text{H}_2\text{O}\,(l) \quad E°_{cell} = -0.20\,V$$

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:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E°cell = 1.10V \tag{20.4.7}$$

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 20.4.6:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \tag{20.4.8}$$

$$= 1.10\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right) \log \left(\frac{1.0 \times 10^{-6}}{1.0}\right) = 1.28\ \text{V} \tag{20.4.9}$$

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.

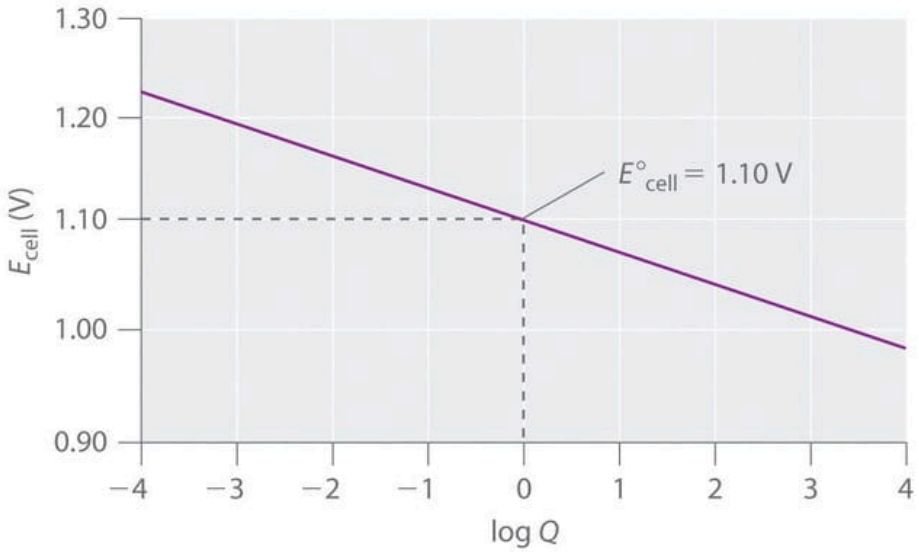


Figure 20.4.1: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than E°$_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When [Zn^{2+}] = [Cu^{2+}], log Q = 0 and E_{cell} = E°$_{cell}$ = 1.10 V. As long 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 20.4.1. 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:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q = 0 \tag{20.4.10}$$

$$E^{\circ} = \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{20.4.11}$$

$$\log Q = \frac{E^{\circ} n}{0.0591\ \text{V}} = \frac{(1.10\ \text{V})(2)}{0.0591\ \text{V}} = 37.23 \tag{20.4.12}$$

$$Q = 10^{37.23} = 1.7 \times 10^{37} \tag{20.4.13}$$

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

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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:

$$\mathrm{Ag(s)\,|\,Ag^+}(aq, 0.010\ M)\,||\,\mathrm{Ag^+}(aq, 1.0\ M)\,|\,\mathrm{Ag\,(s)} \tag{20.4.14}$$

cathode:

$$\mathrm{Ag^+}(aq, 1.0\ M) + \mathrm{e^-} \rightarrow \mathrm{Ag\,(s)} \tag{20.4.15}$$

anode:

$$\mathrm{Ag\,(s)} \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) + \mathrm{e^-} \tag{20.4.16}$$

Overall

$$\mathrm{Ag^+}(aq, 1.0\ M) \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) \tag{20.4.17}$$

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 20.4.2

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 20.4.6:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log Q \\ &= 0\text{ V} - \left(\frac{0.0591\text{ V}}{2}\right)\log\left(\frac{5.2 \times 10^{-2}}{2.0}\right) \\ &= 0.047\text{ V} \end{aligned}$$

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 20.4.2

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:

$$\mathrm{O_2\,(g) + 4\,H^+\,(aq) + 4\,e^-} \rightarrow \mathrm{2\,H_2O\,(l)}$$

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.

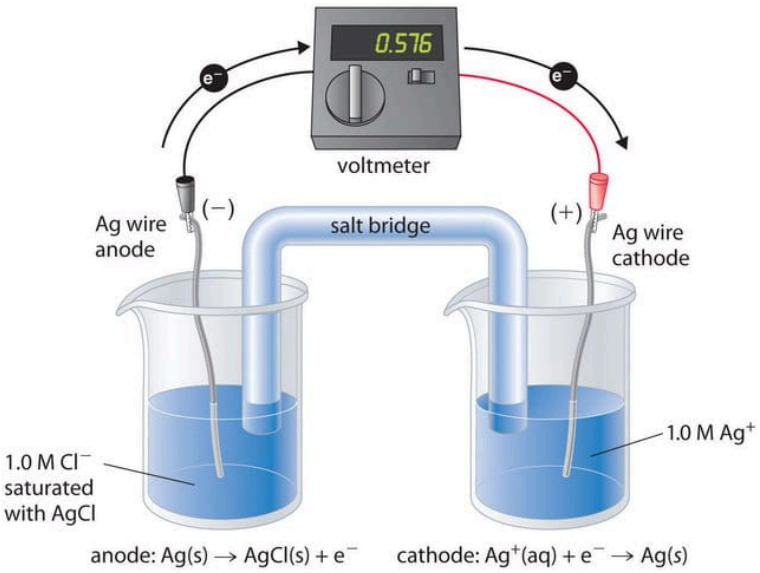


Figure 20.4.1: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to 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 20.4.1, 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:

$$\begin{aligned}E_{\text{cell}} &= 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{1}\right)\log\left(\frac{[\mathrm{Ag^+}]_{\text{dilute}}}{[\mathrm{Ag^+}]_{\text{concentrated}}}\right) \\ &= -0.0591\ \text{V}\ \log\left(\frac{K_{\text{sp}}}{1.0}\right) \\ &= -0.0591\ \text{V}\ \log K_{\text{sp}}\end{aligned} \tag{20.4.18}$$

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 20.4.18 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 20.4.3: 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 20.4.1, 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 20.4.3

A concentration cell similar to the one described in Example 20.4.3 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 20.4.3, 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 20.4.4: 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 20.4.6), we can calculate $[H^+]$ under nonstandard conditions:

$$E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - \left(\frac{0.0591\ \mathrm{V}}{n}\right)\log\left(\frac{[\mathrm{Zn^{2+}}]P_{\mathrm{H_2}}}{[\mathrm{H^+}]^2}\right)$$

$$0.26\ \mathrm{V} = 0.76\ \mathrm{V} - \left(\frac{0.0591\ \mathrm{V}}{2}\right)\log\left(\frac{(1.0)(1.0)}{[\mathrm{H^+}]^2}\right)$$

$$16.9 = \log\left(\frac{1}{[\mathrm{H^+}]^2}\right) = \log[\mathrm{H^+}]^{-2} = (-2)\log[\mathrm{H^+}]$$

$$8.46 = -\log[\mathrm{H^+}]$$

$$8.5 = \mathrm{pH}$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise 20.4.4

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 20.4.1

E_{cell} = −0.22 V; the reaction will not occur spontaneously.

Exercise 20.4.2

0.41 V

Exercise 20.4.3

5.7×10^{-17}

Exercise 20.4.4

$1.2 \times 10^{-9}\ M$

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20.5: Batteries: Producing Electricity Through Chemical Reactions

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 20.5.1). 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.

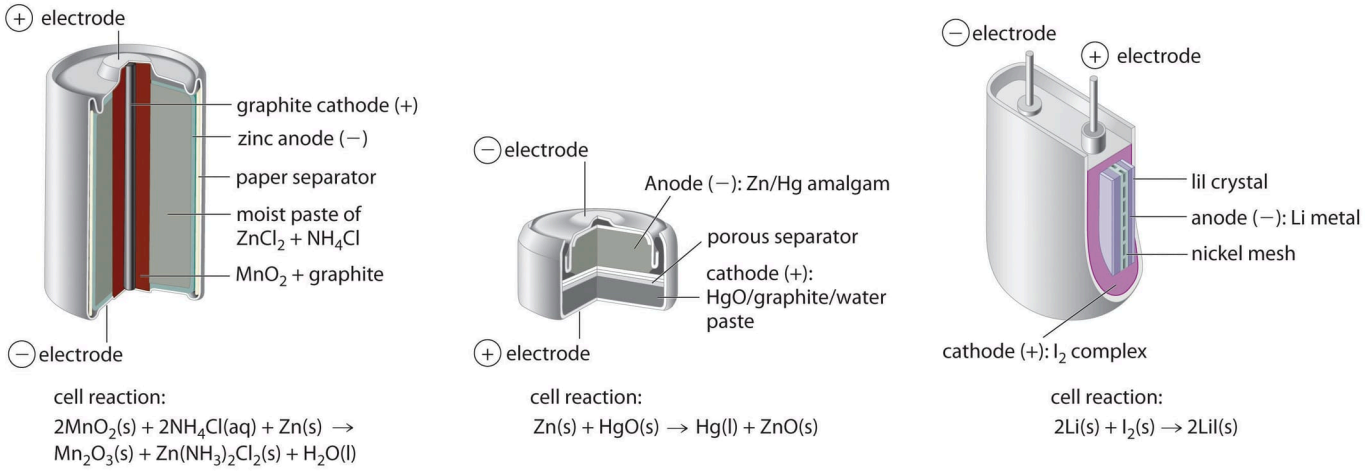


Figure 20.5.1: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in 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 $20.5.1$). 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:

$$2\,\mathrm{MnO_2\,(s)} + 2\,\mathrm{NH_4Cl\,(aq)} + \mathrm{Zn\,(s)} \longrightarrow \mathrm{Mn_2O_3\,(s)} + \mathrm{Zn(NH_3)_2Cl_2\,(s)} + \mathrm{H_2O\,(l)} \tag{20.5.1}$$

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
battery" style="width: 287px; height: 215px;" width="287px" height="215px" data-cke-saved-src="/@api/deki/files/16647/battery.jpg" src="/@api/deki/files/16647/battery.jpg" data-quail-id="34">

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 $20.5.1b$).



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 $\mathrm{Li^+}$ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-{}_{(LiI)} \tag{20.5.2}$$

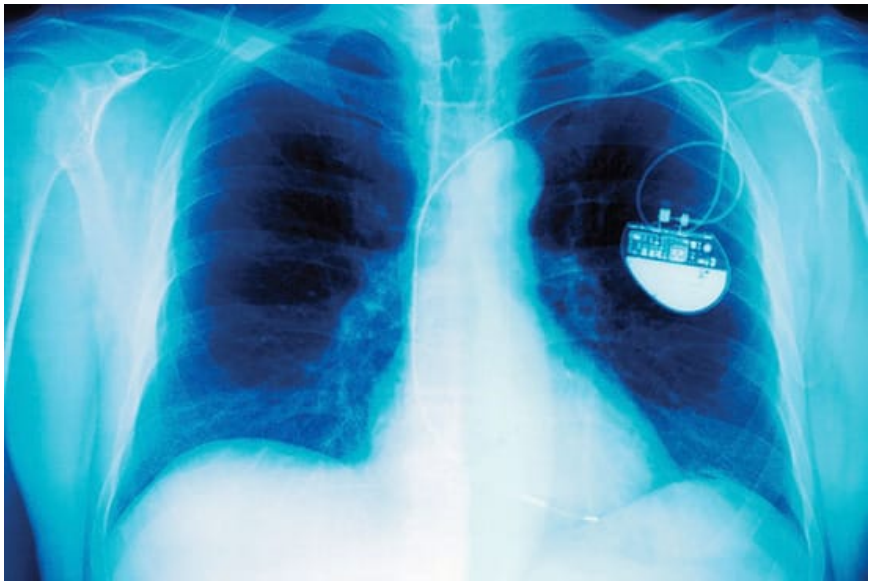
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{20.5.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{20.5.4}$$

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 $20.5.1$, 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 $20.5.2$, 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.

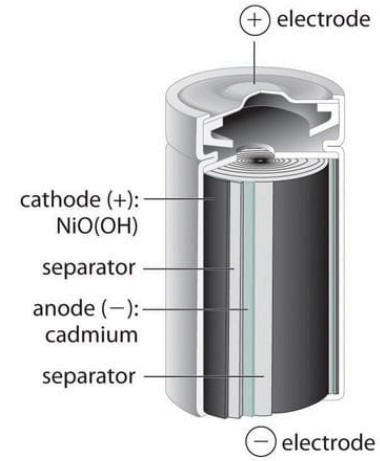


Figure 20.5.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a $NiCad$ battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{20.5.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{20.5.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{20.5.7}$$

$$E_{cell} = 1.4V$$

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.

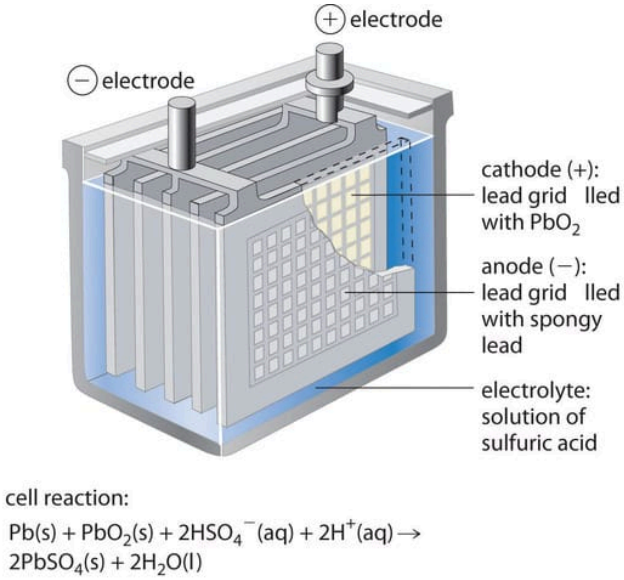


Figure 20.5.3: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value 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 20.5.3, 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):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{20.5.8}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{20.5.9}$$

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.

View this YouTube Video online

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:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{20.5.10}$$

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.

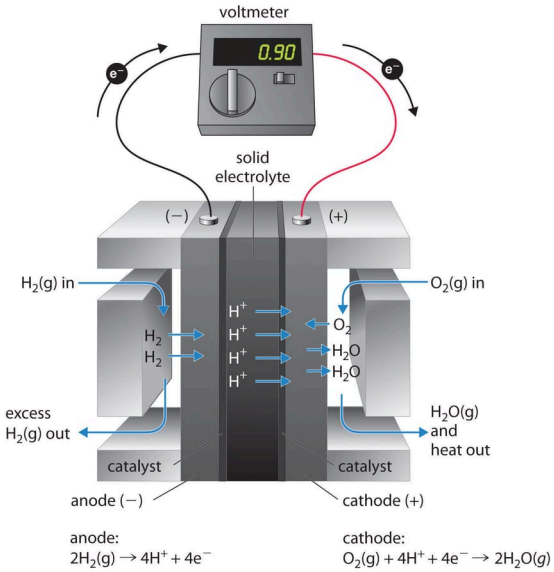


Figure 20.5.4: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte 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 20.5.4. The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{20.5.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{20.5.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{20.5.13}$$

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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20.6: Corrosion: Unwanted Voltaic Cells

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 $20.6.1$). 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.

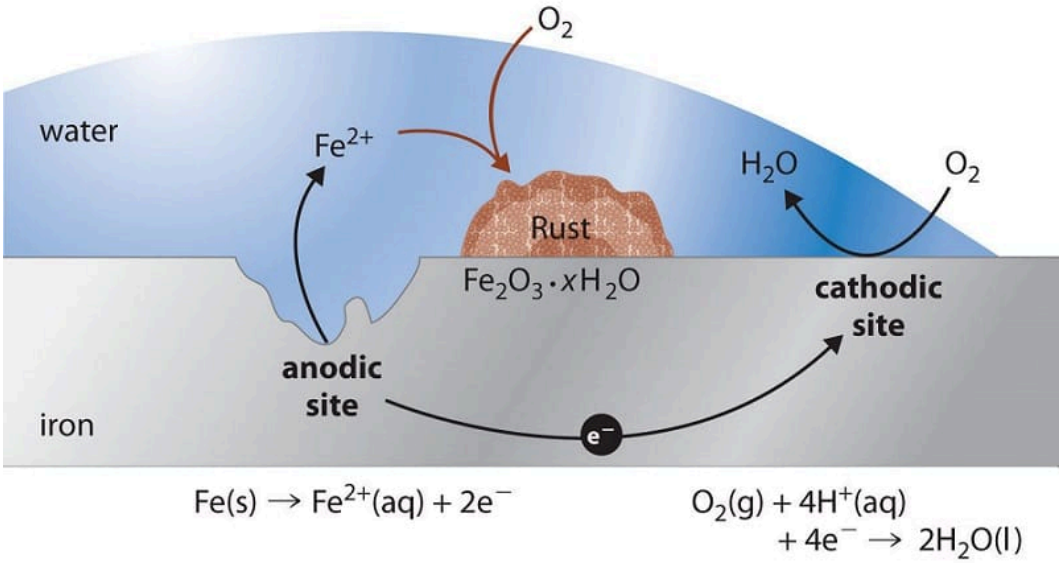


Figure $20.6.1$: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to $Fe^{2+}(aq)$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons 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:

$$\mathrm{2\,Fe\,(s) + O_2\,(g) + 4\,H^+\,(aq) \longrightarrow 2\,Fe^{2+}\,(aq) + 2\,H_2O\,(l)} \tag{20.6.1}$$

  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:

$$\mathrm{4\,Fe^{2+}\,(aq) + O_2\,(g) + (2 + 4\,x)H_2O \ \rightarrow 2\,Fe_2O_3 \ \cdot x\,H_2O + 4\,H^+\,(aq)} \tag{20.6.2}$$

The sign and magnitude of E^o_{cell} for the corrosion process (Equation 20.6.1) 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 20.6.2).

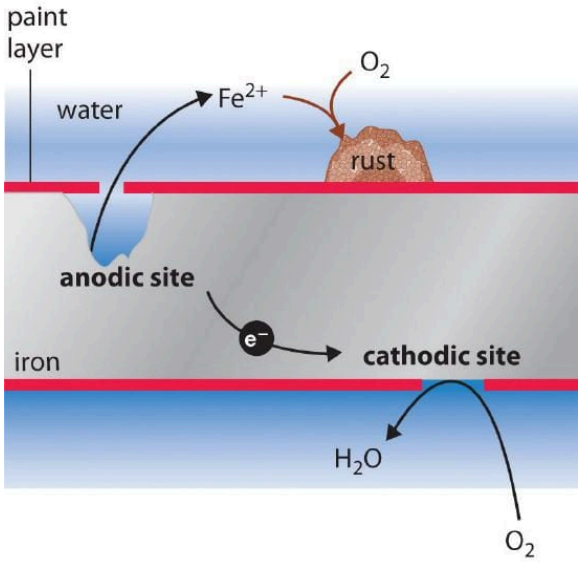


Figure 20.6.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). 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).

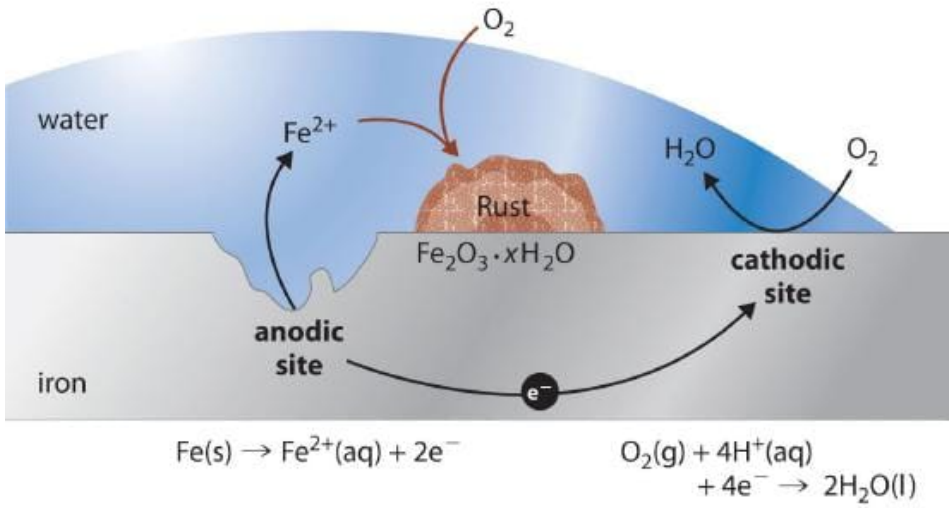


Figure 20.6.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can 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 20.6.3). 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:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{20.6.3}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{20.6.4}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{20.6.5}$$

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 20.6.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

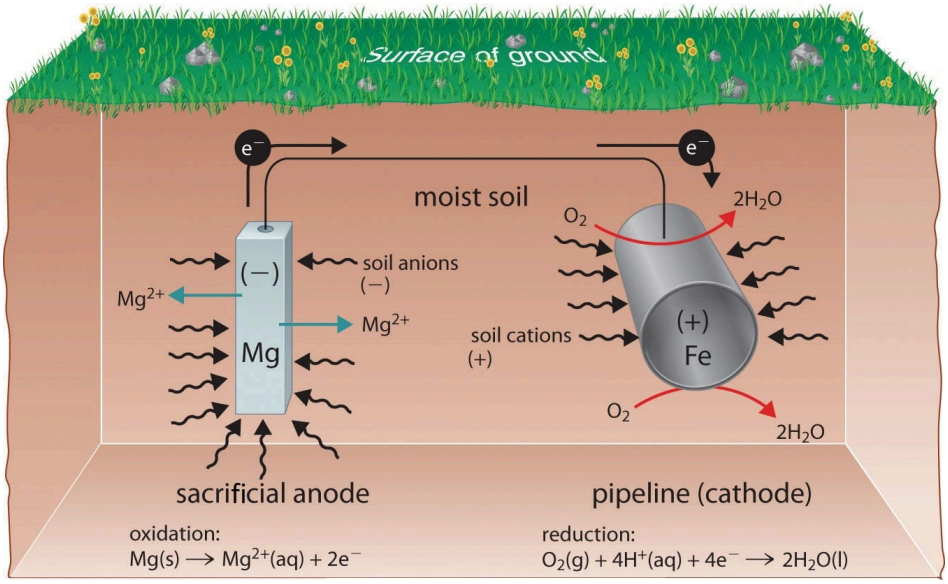


Figure 20.6.4: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium ($E° = -2.37$ V) is much more easily oxidized than iron ($E° = -0.45$ V), the Mg rod acts as the anode in 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 20.6.1

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 20.6.5).



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 20.6.1

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 $20.6.1$

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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20.7: Electrolysis: Causing Nonspontaneous Reactions to Occur

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 $20.7.1a$).

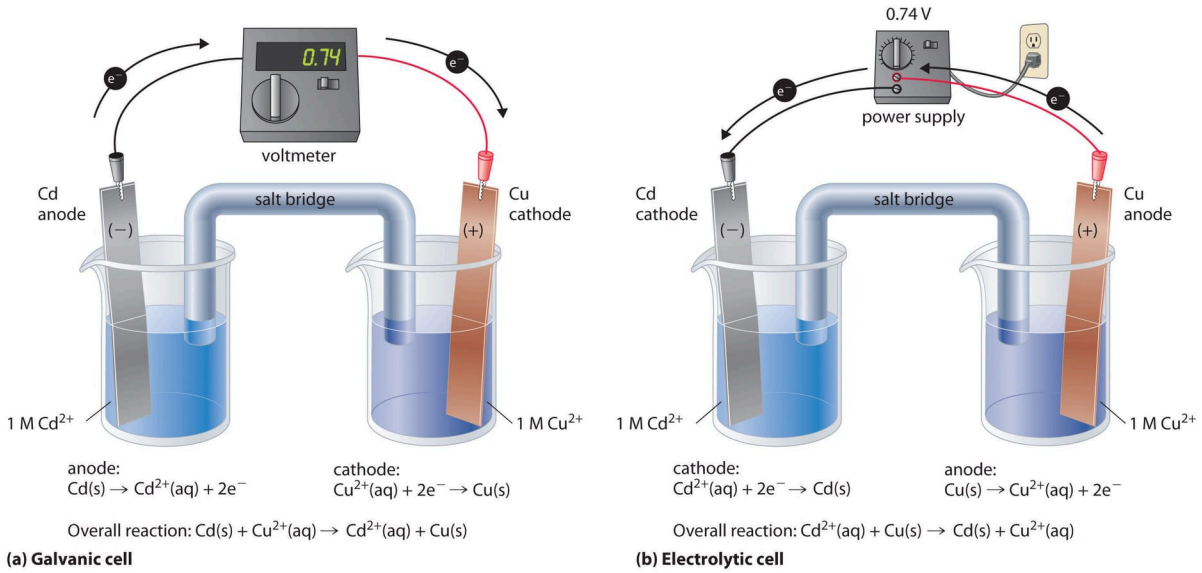


Figure $20.7.1$: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) 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 $20.7.1b$). 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:

$$\text{Cd}^{2+}\,(\text{aq}) + 2\,\text{e}^- \rightarrow \text{Cd}\,(\text{s}) \tag{20.7.1}$$

with $E^\circ_{cathode} = -0.40\ V$

- half-reaction at the anode:

$$\text{Cu}\,(\text{s}) \rightarrow \text{Cu}^{2+}\,(\text{aq}) + 2\,\text{e}^- \tag{20.7.2}$$

with $E^\circ_{anode} = 0.34\ V$

- Overall Reaction:

$$\text{Cd}^{2+}\,(\text{aq}) + \text{Cu}\,(\text{s}) \rightarrow \text{Cd}\,(\text{s}) + \text{Cu}^{2+}\,(\text{aq}) \tag{20.7.3}$$

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 $20.7.1$.

Table $20.7.1$: 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:

$$2\,NaCl\,(l) \rightarrow 2\,Na\,(l) + Cl_2\,(g) \tag{20.7.4}$$

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 20.7.2). In this specialized cell, $CaCl_2$ (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.

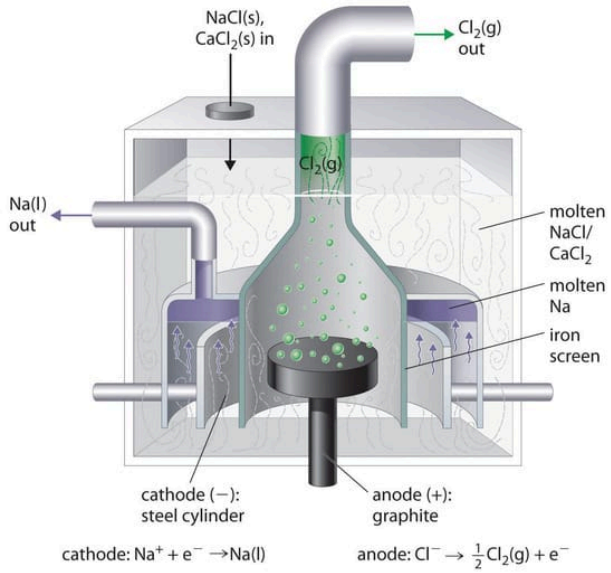


Figure 20.7.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the 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:

$$2\,Al_2O_3\,(l) + 3\,C\,(s) \longrightarrow 4\,Al\,(l) + 3\,CO_2\,(g) \tag{20.7.5}$$

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 20.7.1

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 20.7.1

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 20.7.3).

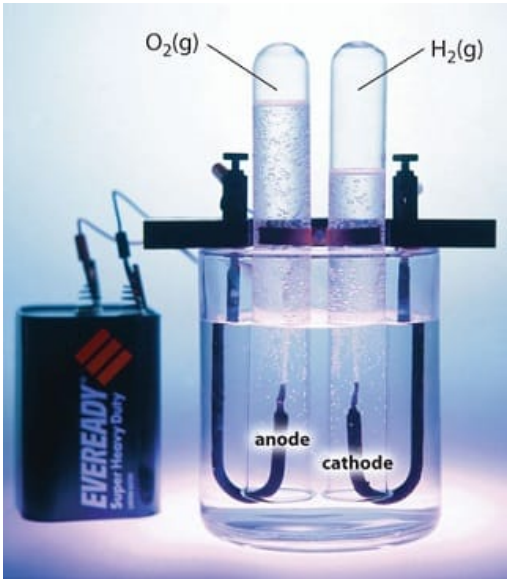


Figure 20.7.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{20.7.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{20.7.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{20.7.8}$$

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:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log(P_{O_2}P^2_{H_2}) \tag{20.7.9}$$

$$= -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right)\log(1) = -1.23\ \text{V} \tag{20.7.10}$$

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 $20.7.4$.

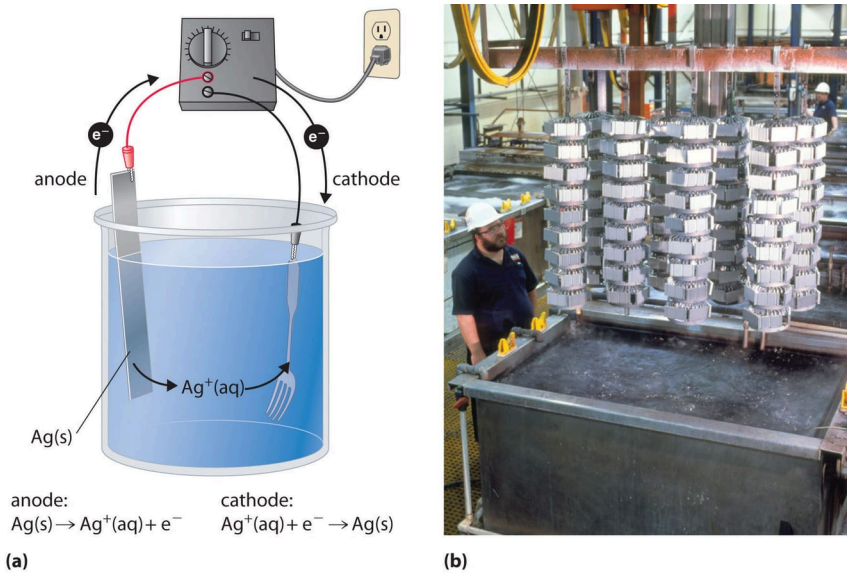


Figure $20.7.3$: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode 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 $\mathrm{Ag^+}$ 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):

$$\mathrm{Ag^+\,(aq) + e^- \longrightarrow Ag\,(s)} \qquad E°_{cathode} = 0.80V$$

- anode (silver bar):

$$\mathrm{Ag\,(s) \longrightarrow Ag^+\,(aq) + e^-} \qquad E°_{anode} = 0.80V$$

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):

$$q = I \times t \tag{20.7.11}$$

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 20.7.2

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 20.7.2

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 20.7.1

Br_2 and Al

Exercise 20.7.2

5.8 h

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20.8: Industrial Electrolysis Processes

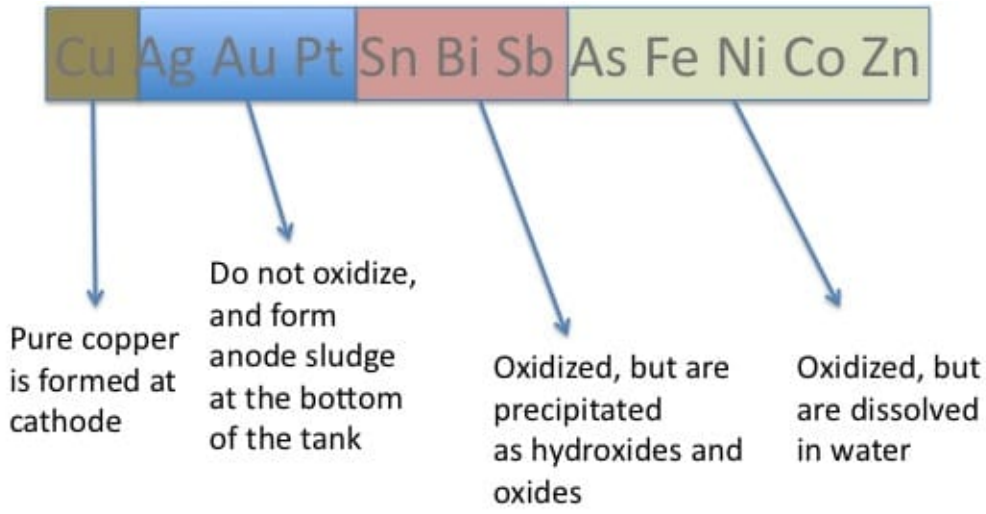
Learning Objectives

- Define Electrorefining and electrosynthesis
- Explain the basics of the industrial electrolysis of salt water to generate chlorine gas.

Electrolysis reactions are the basic foundations of today's modern industry. There are various elements, chemical compounds, and organic compounds that are only produced by electrolysis including aluminum, chlorine, and NaOH. Electrolysis is the process by which an electric current spurs an otherwise non-spontaneous reaction.

Electrorefining

The electrorefining process refines metals or compounds at a high purity for a low cost. The pure metal can coat an otherwise worthless object. Let's consider the electrorefining process of copper: At the anode, there is an impure piece of copper that has other metals such as Ag, Au, Pt, Sn, Bi, Sb, As, Fe, Ni, Co, and Zn. The copper in this impure ore is oxidized to form Cu^{2+} at the anode, and moves through an aqueous sulfuric acid-Copper (II) sulfate solution into the cathode. When it reaches the cathode, the Cu^{2+} is reduced to Cu. This whole process takes place at a fairly low voltage (about .15 to .30 V), so Ag, Au, and Pt are not oxidized at the anode, as their standard oxidation electrode potentials are -.800, -1.36 and -1.20 respectively; these unoxidized impurities turn into a mixture called anode mud, a sludge at the bottom of the tank. This sludge can be recovered and used in different processes. Unlike Ag, Au and Pt, the impurities of Sb, Bi and Sn in the ore are indeed oxidized at the anode, but they are precipitated as they form hydroxides and oxides. Finally, Fe, Ni, Co and Zn are oxidized as well, but they are dissolved in water. Therefore, the only solid we are left with is the pure solid copper plate at the cathode, which has a purity level of about 99.999%. The image below gives an outline about the fate of the main components of an impure iron ore.



Electrosynthesis

Electrosynthesis is the method of producing substances through electrolysis reactions. This is useful when reaction conditions must be carefully controlled. One example of electrosynthesis is that of MnO_2, Manganese dioxide. MnO_2 occurs naturally in the form of the mineral pyrolusite, but this mineral is not easily used due to the nature of its size and lattice structure. However, MnO_2 can be obtained a different way, through the electrolysis of $MnSO_4$ in a sulfuric acid solution.

$$\text{Oxidation:} \quad \mathrm{Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-} \quad \mathrm{E^0_{MnO_2/H_2} = -1.23} \tag{20.8.1}$$

$$\text{Reduction:} \quad \mathrm{2e^- + 2H^+ \rightarrow H_2} \quad \mathrm{-E^0_{H^+/H_2} = -0} \tag{20.8.2}$$

$$\text{Overall:} \quad \mathrm{Mn^{2+} + 2H_2O \rightarrow MnO_2 + 2H^+ + H_2} \quad \mathrm{E^0_{MnO_2/H_2} - E^0_{H^+/H_2} = -1.23 - 0 = -1.23} \tag{20.8.3}$$

The commercial process for organic chemicals that is currently practiced on a scale comparable to that of inorganic chemicals and metals is the electrohydrodimerization of acrylonitrile to adiponitrile.

$$\text{Anode:} \quad \mathrm{H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-} \tag{20.8.4}$$

$$\text{Cathode:} \quad \mathrm{2\,CH_2{=}CHCN + 2\,H_2O + 2\,e^- \rightarrow NC(CH_2)CN + 2\,OH^-} \tag{20.8.5}$$

$$\text{Overall:} \quad \underset{\text{acrylonitrile}}{\mathrm{2\,CH_2{=}CHCN}} + H_2O \rightarrow \frac{1}{2}O_2 + \underset{\text{adiponitrile}}{\mathrm{NC(CH_2)_4CN}} \tag{20.8.6}$$

The importance of adiponitrile is that it can be readily converted to other useful compounds.

The Chlor-Alkali Process

This process is the electrolysis of sodium chloride (NaCl) at an industrial level. We will begin by discussing the equation for the chlor-alkali process, followed by discussing three different types of the process: the diaphragm cell, the mercury cell and the membrane cell. We will begin the explanation of the chlor-alkali process by determining the reactions that occur during the electrolysis of NaCl. Because NaCl is in an aqueous solution, we also have to consider the electrolysis of water at both the anode and the cathode. Therefore, there are two possible reduction equations and two possible oxidation reactions.

Reduction:

$$\mathrm{Na^+_{(aq)} + 2e^- \rightarrow Na_{(s)}} \quad \mathrm{E^0_{Na^+/Na} = -2.71\ V} \tag{20.8.7}$$

$$\mathrm{2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}} \quad \mathrm{E^0_{H_2O/H_2} = -0.83\ V} \tag{20.8.8}$$

Oxidation:

$$\mathrm{2Cl^-_{(aq)} \rightarrow Cl_2 + 2e^-} \quad \mathrm{-E^0_{Cl_2/Cl^-} = -1.36\ V} \tag{20.8.9}$$

$$\mathrm{2H_2O_{(l)} \rightarrow O_2 + 4H^+ + 4e^-} \quad \mathrm{-E^0_{O_2/H_2O} = -1.23\ V} \tag{20.8.10}$$

As we can see, due to the very much more negative electrode potential, the reduction of sodium ions is much less likely to occur than the reduction of water, so we can assume that in the electrolysis of NaCl, the reduction that occurs is Equation 20.8.8. Therefore, we should try to determine what the oxidation reaction that occurs is.

Let's say we have Equation 20.8.8 as the reduction and Equation 20.8.9 as the oxidation. We would get:

$$\text{Reduction:} \quad \mathrm{2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}} \quad \mathrm{E^0_{H_20/H_2} = -0.83\ V} \tag{20.8.11}$$

$$\text{Oxidation:} \quad \mathrm{2Cl^-_{(aq)} \rightarrow Cl_2 + 2e^-} \quad \mathrm{-E^0_{Cl_2/Cl^-} = -(1.36\ V)} \tag{20.8.12}$$

$$\text{Overall:} \quad \mathrm{2H_2O_{(l)} + 2Cl^-_{(aq)}} \quad \mathrm{E^0_{H_20/H_2} - E^0_{Cl_2/Cl^-}} \tag{20.8.13}$$

$$\mathrm{\rightarrow H_{2(g)} + 2OH^-_{(aq)} + Cl_2} \quad \mathrm{= -0.83 + (-1.36) = -2.19} \tag{20.8.14}$$

Alternatively, we could also have Equation 20.8.8 with 20.8.10

$$\text{Reduction:} \quad \mathrm{2\,[2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}]} \quad \mathrm{E_{H_2O/H_2O} = -.83\ V} \tag{20.8.15}$$

$$\text{Oxidation:} \quad \mathrm{2H_2O_{(l)} \rightarrow O_2 + 4H^+ + 4e^-} \quad \mathrm{-E^0_{O_2/H_20} = -(1.23\ V)} \tag{20.8.16}$$

$$\text{Overall:} \quad \mathrm{2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}} \quad \mathrm{E^0_{H_2O/H_2} - E^0_{O_2/H_20}} \tag{20.8.17}$$

$$\mathrm{= -0.83\ V - (1.23\ V) = -2.06} \tag{20.8.18}$$

At first glance it would appear as though Equation 20.8.17 would occur due to the smaller (less negative) electrode potential. However, O_2 actually has a fairly large overpotential, so instead Cl_2 is more likely to form, making Equation 20.8.13 the most probable outcome for the electrolysis of NaCl.

Chlor-Alkali Process in a Diaphragm Cell

Depending on the method used, there can be several different products produced through the chlor-alkali process. The value of these products is what makes the chlor-alkali process so important. The name comes from the two main products of the process, chlorine and the alkali, sodium hydroxide (NaOH). Therefore, one of the main uses of the chlor-alkali process is the production of NaOH. As described earlier, the equation for the chlor-alkali process, that is, the electrolysis of NaCl, is as follows:

$$\text{Reduction:} \quad 2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \qquad E_{H_2O/H_2O} = -0.83\ V \tag{20.8.19}$$

$$\text{Oxidation:} \quad 2Cl^-_{(aq)} \rightarrow Cl_2 + 2e^- \qquad E^0_{Cl_2/Cl^-} = -1.36\ V \tag{20.8.20}$$

$$\text{Overall:} \quad 2Cl^- + 2H_2O_{(l)} \rightarrow 2OH^- + H_{2(g)} + Cl_{2(g)} \qquad E^0_{H_2O/H_2} - E^0_{Cl/Cl_2^-} \tag{20.8.21}$$

$$= -0.83\ V - (-1.36\ V) = -2.19\ V \tag{20.8.22}$$

**The chlor-alkali process often occurs in an apparatus called a diaphragm cell, which is illustrated in Figure 20.8.1.

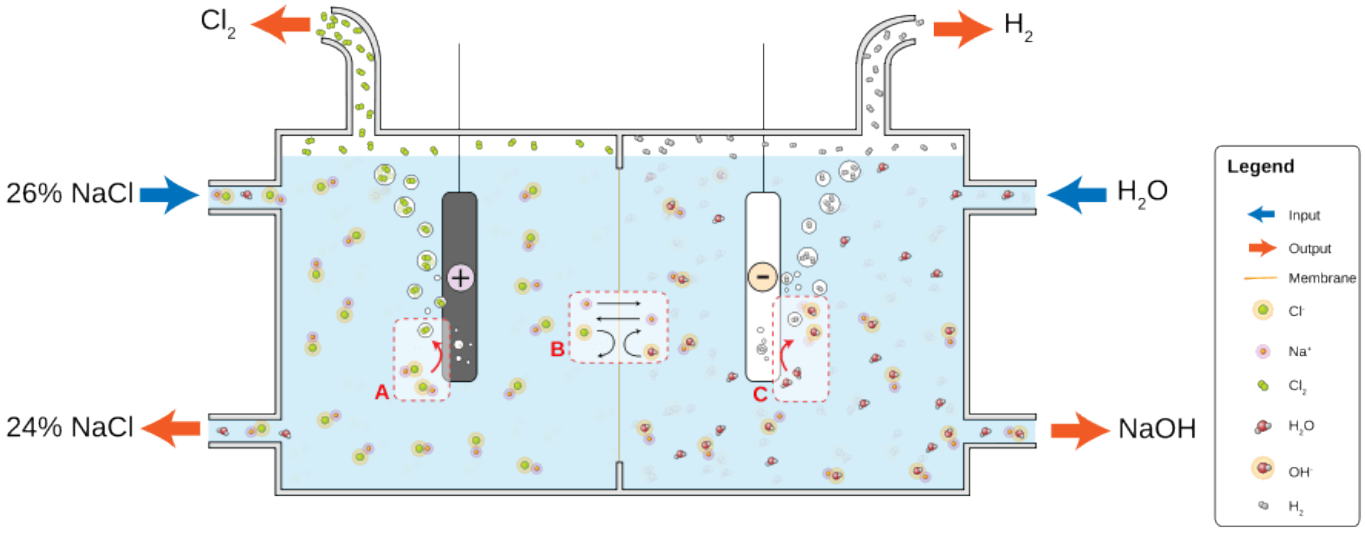


Figure 20.8.1***:*** *Basic membrane cell used in the electrolysis of brine. At the anode (**A**), chloride (Cl^-) is oxidized to chlorine. The ion-selective membrane (**B**) allows the counterion Na+ to freely flow across, but prevents anions such as hydroxide (OH^-) and chloride from diffusing across. At the cathode (**C**), water is reduced to hydroxide and hydrogen gas. The net process is the electrolysis of an aqueous solution of NaCl into industrially useful products sodium hydroxide (NaOH) and chlorine gas. of Wikipedia (Jkwchui)*

Note the following aspects of the Diagram cell:

Anode

- The sodium chloride is put into the anode compartment, in aqueous form.
- The actual physical anode is made of either graphite or titanium.
- In the anode compartment, Cl_2 gas is produced as Cl^- is oxidized.

Cathode

- On the cathode side, OH^- (aq) and H_2 gas are formed as water is reduced.
- You may wonder, why are there sodium and chloride ions of the cathode side if we put the sodium chloride into the anode compartment? To answer this question, we can consider the difference in solution levels between the anode and cathode. This causes the gradual flow of NaCl into the cathode, and prevents the backflow of NaOH into the anode. If Cl_2 and NaOH come into contact, Cl_2 turns into ClO^-, ClO_3^-, Cl^- ions. The water level difference prevents this contact and also encourages the flow of NaCl to the cathode side, so NaOH (aq) can form.
- Now, you may notice that the solution with NaOH in the cathode will also have aqueous NaCl mixed with it due to the flow of NaCl from the anode to the cathode. Therefore, if we want very pure NaOH for uses such as rayon manufacture, we need to

somehow purify the salt out of the NaOH. In general, before purification, the solution is about 14-16% NaCl (aq) and 10-12% NaOH (aq). However, the NaOH (aq) can be concentrated and the NaCl (s) can be crystallized to form a solution with 50% NaOH (aq) and about 1% NaCl (aq).

Note

If chlorine comes into contact with hydrogen, it produces a mixture which will explode violently on exposure to sunlight or heat. Hydrogen chloride gas would be produced. Obviously, the two gases need to be kept apart.

Chlor-Alkali Process in Mercury Cell

To even further improve the purity of NaOH, a mercury cell can be used for the location of electrolysis, opposed to a diaphragm cell. In the mercury-cell process, also known as the Castner–Kellner process, a saturated brine solution floats on top of a thin layer of mercury. The mercury is the cathode, where sodium is produced and forms a sodium-mercury amalgam with the mercury. The amalgam is continuously drawn out of the cell and reacted with water which decomposes the amalgam into sodium hydroxide and mercury. The mercury is recycled into the electrolytic cell. Chlorine is produced at the anode and evaporates out of the cell. Mercury cells are being phased out due to concerns about mercury poisoning from mercury cell pollution

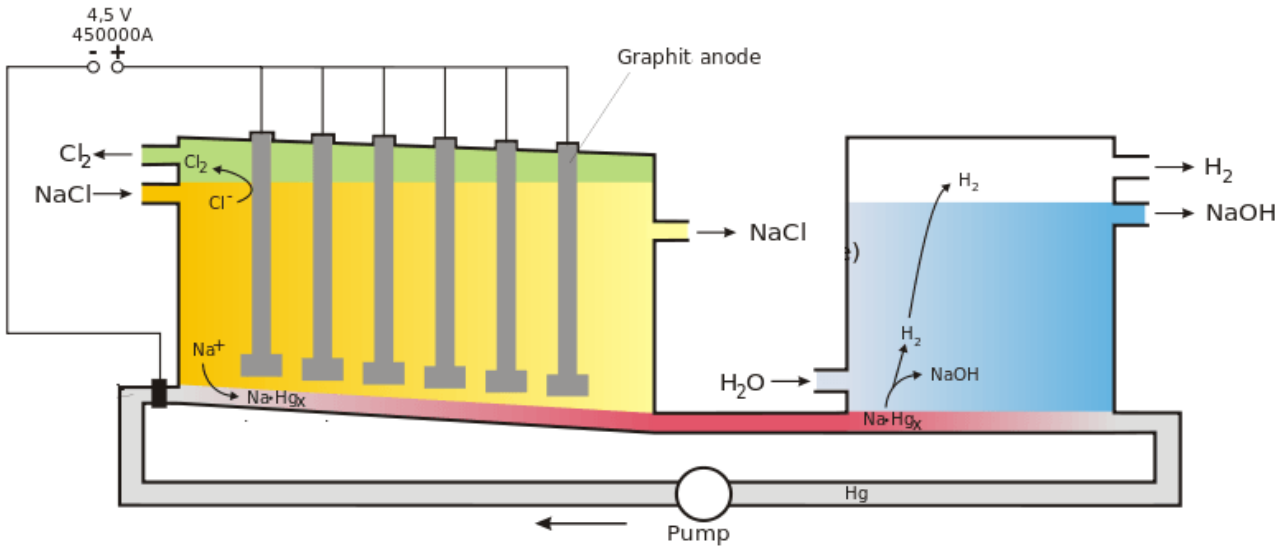


Figure 20.8.2: Mercury cell of the chloralkali process. Image is Public Domain

Anode Side

- The anodes are placed in the aqueous NaCl solution, above the liquid mercury.
- The reduction of Cl^- occurs to produce chlorine gas, Cl_2 (g).

Cathode Side

- A layer of Hg (l) at the bottom of the tank serves as the cathode.
- With a mercury cathode, the reaction of H_2O (l) to H_2 has a fairly high over potential, so the reduction of Na^+ to Na occurs instead. The Na is soluble in Hg (l) and the two combine to form the Na-Hg alloy amalgam. This amalgam can be removed and then mixed with water to cause the following reaction:
  - $2\,\mathrm{Na\,(in\ \ Hg)} + 2\,\mathrm{H_2O} \rightarrow 2\,\mathrm{Na^+} + 2\,\mathrm{OH^-} + \mathrm{H_{2(g)}} + \mathrm{Hg_{(l)}}$
- The Hg (l) that forms is recycled back into the liquid at the bottom of the tank that acts as a cathode.
- H_2 gas is released.
- NaOH is left in a very pure, aqueous form.

****Some of the main problems with the mercury cell are as follows:**

- The reaction needs a higher voltage than the diaphragm cell: 4.5 V in the mercury cell compared to 3.5 in a diaphragm cell.
- Requires quite a bit of electrical energy, as it needs 3400 kWh/ton Cl_2 opposed to 2500 in a diaphragm cell.
- Potential damage to the environment due to mercury deposits. Luckily deposits were as large as 200 g mercury per ton chlorine gas, but now, they never exceed 0.25 g per ton chlorine gas.

Membrane Cell Process

A third way to make even more pure NaOH is to use a membrane cell. It is preferred over the diaphragm cell or mercury cell method because it uses the least amount of electric energy and produces the highest quality NaOH. For instance, it can produce NaOH with a degree of chlorine ion contamination of only 50 ppm. An ion-permeable membrane is used to separate the anode and cathode.

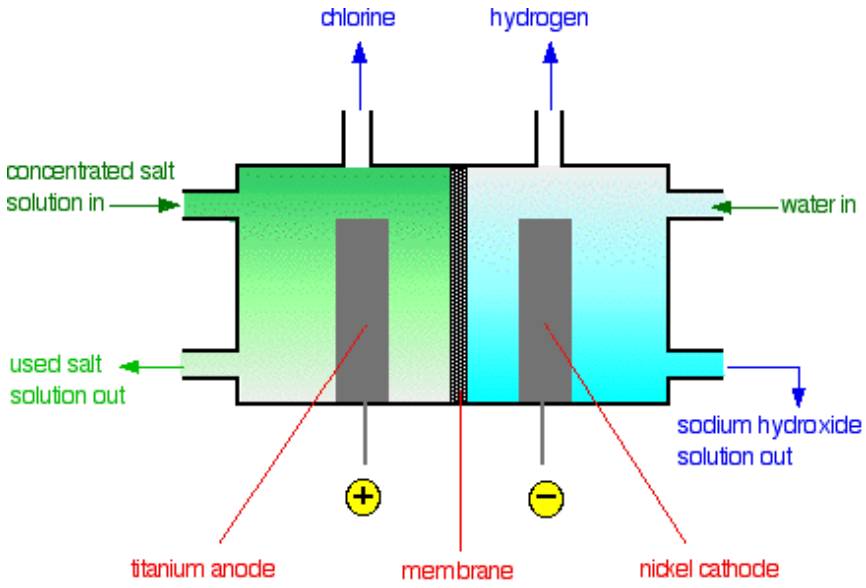


Figure 20.8.3: This is a simplification of a real cell to show the main features. You will find other diagrams with the inlets and outlets in different places or in more detail.

Anode

Saturated brine is fed to the compartment. Current passed through the cell splits the sodium chloride into its constituent components, Na^+ and Cl^-. Chloride ions are oxidized to chlorine gas at the anode.

$$2Cl^-_{(aq)} \rightarrow 2e^- + Cl_{2(g)} \tag{20.8.23}$$

The chlorine is purified by liquifying it under pressure. The oxygen stays as a gas when it is compressed at ordinary temperatures. The membrane passes Na^+ ions to the cathode compartment.

Cathode

The hydrogen is produced at the nickel cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \tag{20.8.24}$$

- H_2O is reduced to form OH^- and H_2 gas.
  - $2\,H_2O \rightarrow H_2 + 2\,OH^-$
- Na^+ ions that had flowed over and OH^- produced through the reduction of water react to form aqueous NaOH.
- H_2 gas also is produced as a byproduct.

The membrane is made from a polymer which only allows positive ions to pass through it. That means that the only the sodium ions from the sodium chloride solution can pass through the membrane - and not the chloride ions. The advantage of this is that

the sodium hydroxide solution being formed in the right-hand compartment never gets contaminated with any sodium chloride solution. The sodium chloride solution being used has to be pure. If it contained any other metal ions, these would also pass through the membrane and so contaminate the sodium hydroxide solution.

References

- General Chemistry, Principles & modern Applications, Petrucci, 2007, 2002, 1997

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- Jim Clark (Chemguide.co.uk)
- Wikipedia

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20.E: Exercises

20.1: Electrode Potentials and their Measurement

Conceptual Problems

1. Is $2NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$ an oxidation–reduction reaction? Why or why not?
2. If two half-reactions are physically separated, how is it possible for a redox reaction to occur? What is the name of the apparatus in which two half-reactions are carried out simultaneously?
3. What is the difference between a galvanic cell and an electrolytic cell? Which would you use to generate electricity?
4. What is the purpose of a salt bridge in a galvanic cell? Is it always necessary to use a salt bridge in a galvanic cell?
5. One criterion for a good salt bridge is that it contains ions that have similar rates of diffusion in aqueous solution, as K^+ and Cl^- ions do. What would happen if the diffusion rates of the anions and cations differed significantly?
6. It is often more accurate to measure the potential of a redox reaction by immersing two electrodes in a single beaker rather than in two beakers. Why?

Conceptual Answer

5. A large difference in cation/anion diffusion rates would increase resistance in the salt bridge and limit electron flow through the circuit.

1. Numerical Problems

1. Copper(I) sulfate forms a bright blue solution in water. If a piece of zinc metal is placed in a beaker of aqueous $CuSO_4$ solution, the blue color fades with time, the zinc strip begins to erode, and a black solid forms around the zinc strip. What is happening? Write half-reactions to show the chemical changes that are occurring. What will happen if a piece of copper metal is placed in a colorless aqueous solution of $ZnCl_2$?
2. Consider the following spontaneous redox reaction: $NO_3^-(aq) + H^+(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + HNO_2(aq)$.

    a. Write the two half-reactions for this overall reaction.
    b. If the reaction is carried out in a galvanic cell using an inert electrode in each compartment, which electrode corresponds to which half-reaction?
    c. Which electrode is negatively charged, and which is positively charged?

3. The reaction $Pb(s) + 2VO^{2+}(aq) + 4H^+(aq) \rightarrow Pb^{2+}(aq) + 2V^{3+}(aq) + 2H_2O(l)$ occurs spontaneously.

    a. Write the two half-reactions for this redox reaction.
    b. If the reaction is carried out in a galvanic cell using an inert electrode in each compartment, which reaction occurs at the cathode and which occurs at the anode?
    c. Which electrode is positively charged, and which is negatively charged?

4. Phenolphthalein is an indicator that turns pink under basic conditions. When an iron nail is placed in a gel that contains $[Fe(CN)_6]^{3-}$, the gel around the nail begins to turn pink. What is occurring? Write the half-reactions and then write the overall redox reaction.

5. Sulfate is reduced to HS^- in the presence of glucose, which is oxidized to bicarbonate. Write the two half-reactions corresponding to this process. What is the equation for the overall reaction?

6. Write the spontaneous half-reactions and the overall reaction for each proposed cell diagram. State which half-reaction occurs at the anode and which occurs at the cathode.

    a. $Pb(s)|PbSO_4(s)|SO_4^{2-}(aq)||Cu^{2+}(aq)|Cu(s)$

b. $Hg(l)|Hg_2Cl_2(s)|Cl^-(aq) \parallel Cd^{2+}(aq)|Cd(s)$

7. For each galvanic cell represented by these cell diagrams, determine the spontaneous half-reactions and the overall reaction. Indicate which reaction occurs at the anode and which occurs at the cathode.

   a. $Zn(s)|Zn^{2+}(aq) \parallel H^+(aq)|H_2(g), Pt(s)$
   b. $Ag(s)|AgCl(s)|Cl^-(aq) \parallel H^+(aq)|H_2(g)|Pt(s)$
   c. $Pt(s)|H_2(g)|H^+(aq) \parallel Fe^{2+}(aq), Fe^{3+}(aq)|Pt(s)$

8. For each redox reaction, write the half-reactions and draw the cell diagram for a galvanic cell in which the overall reaction occurs spontaneously. Identify each electrode as either positive or negative.

   a. $Ag(s) + Fe^{3+}(aq) \rightarrow Ag^+(aq) + Fe^{2+}(aq)$
   b. $Fe^{3+}(aq) + 1/2H_2(g) \rightarrow Fe^{2+}(aq) + H^+(aq)$

9. Write the half-reactions for each overall reaction, decide whether the reaction will occur spontaneously, and construct a cell diagram for a galvanic cell in which a spontaneous reaction will occur.

   a. $2Cl^-(aq) + Br_2(l) \rightarrow Cl_2(g) + 2Br^-(aq)$
   b. $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$
   c. $2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$
   d. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

10. Write the half-reactions for each overall reaction, decide whether the reaction will occur spontaneously, and construct a cell diagram for a galvanic cell in which a spontaneous reaction will occur.

    a. $Co(s) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe(s)$
    b. $O_2(g) + 4H^+(aq) + 4Fe^{2+}(aq) \rightarrow 2H_2O(l) + 4Fe^{3+}(aq)$
    c. $6Hg^{2+}(aq) + 2NO_3^-(aq) + 8H^+ \rightarrow 3Hg_2^{2+}(aq) + 2NO(g) + 4H_2O(l)$
    d. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

Numerical Answers

5.

reduction: $SO_4^{2-}(aq) + 9H^+(aq) + 8e^- \rightarrow HS^-(aq) + 4H_2O(l)$

oxidation: $C_6H_{12}O_6(aq) + 12H_2O(l) \rightarrow 6HCO_3^-(g) + 30H^+(aq) + 24e^-$

overall: $C_6H_{12}O_6(aq) + 3SO_4^{2-}(aq) \rightarrow 6HCO_3^-(g) + 3H^+(aq) + 3HS^-(aq)$

7.

a. reduction: $2H^+(aq) + 2e^- \rightarrow H_2(aq)$; cathode;

   oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; anode;

   overall: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(aq)$

b. reduction: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$; cathode;

   oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; anode;

   overall: $AgCl(s) + H_2(g) \rightarrow 2H^+(aq) + Ag(s) + Cl^-(aq)$

c. reduction: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$; cathode;

oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; anode;

overall: $2Fe^{3+}(aq) + H_2(g) \rightarrow 2H^+(aq) + 2Fe^{2+}(aq)$

20.2: Standard Electrode Potentials

Conceptual Problems

1. Is a hydrogen electrode chemically inert? What is the major disadvantage to using a hydrogen electrode?
2. List two factors that affect the measured potential of an electrochemical cell and explain their impact on the measurements.
3. What is the relationship between electron flow and the potential energy of valence electrons? If the valence electrons of substance A have a higher potential energy than those of substance B, what is the direction of electron flow between them in a galvanic cell?
4. If the components of a galvanic cell include aluminum and bromine, what is the predicted direction of electron flow? Why?
5. Write a cell diagram representing a cell that contains the Ni/Ni^{2+} couple in one compartment and the SHE in the other compartment. What are the values of $E°_{cathode}$, $E°_{anode}$, and $E°_{cell}$?
6. Explain why E° values are independent of the stoichiometric coefficients in the corresponding half-reaction.
7. Identify the oxidants and the reductants in each redox reaction.

   a. $Cr(s) + Ni^{2+}(aq) \rightarrow Cr^{2+}(aq) + Ni(s)$
   b. $Cl_2(g) + Sn^{2+}(aq) \rightarrow 2Cl^-(aq) + Sn^{4+}(aq)$
   c. $H_3AsO_4(aq) + 8H^+(aq) + 4Zn(s) \rightarrow AsH_3(g) + 4H_2O(l) + 4Zn^{2+}(aq)$
   d. $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$

8. Identify the oxidants and the reductants in each redox reaction.

   a. $Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$
   b. $Cu^{2+}(aq) + 2Ag(s) \rightarrow Cu(s) + 2Ag^+(aq)$
   c. $H^+(aq) + 2MnO_4^-(aq) + 5H_2SO_3(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5HSO_4^-(aq)$
   d. $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(s) + 3H_2O(l)$

9. All reference electrodes must conform to certain requirements. List the requirements and explain their significance.

10. For each application, describe the reference electrode you would use and explain why. In each case, how would the measured potential compare with the corresponding E°?

    a. measuring the potential of a Cl^-/Cl_2 couple
    b. measuring the pH of a solution
    c. measuring the potential of a MnO_4^-/Mn^{2+} couple

Conceptual Answers

5. $Ni(s)|Ni^{2+}(aq)||H^+(aq, 1\ M)|H_2(g, 1\ atm)|Pt(s)$

E°_{anode} E°_{cathode} E°_{cell}	$\mathrm{Ni^{2+}(aq) + 2e^- \rightarrow Ni(s);\ -0.257\ V\ 2H^+(aq) + 2e^- \rightarrow H_2(g);\ 0.000\ V\ 2H^+(aq) + Ni(s) \rightarrow H_2(g) + Ni^{2+}(aq);\ 0.257\ V}$

7.

a. oxidant: $Ni^{2+}(aq)$; reductant: Cr(s)
b. oxidant: $Cl_2(g)$; reductant: $Sn^{2+}(aq)$
c. oxidant: $H_3AsO_4(aq)$; reductant: Zn(s)
d. oxidant: $NO_2(g)$; reductant: $NO_2(g)$

Numerical Problems

1. Draw the cell diagram for a galvanic cell with an SHE and a copper electrode that carries out this overall reaction: $H_2(g) + Cu^{2+}(aq) \rightarrow 2H^+(aq) + Cu(s)$.
2. Draw the cell diagram for a galvanic cell with an SHE and a zinc electrode that carries out this overall reaction: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$.
3. Balance each reaction and calculate the standard electrode potential for each. Be sure to include the physical state of each product and reactant.

   a. $Cl_2(g) + H_2(g) \rightarrow 2Cl^-(aq) + 2H^+(aq)$
   b. $Br_2(aq) + Fe^{2+}(aq) \rightarrow 2Br^-(aq) + Fe^{3+}(aq)$
   c. $Fe^{3+}(aq) + Cd(s) \rightarrow Fe^{2+}(aq) + Cd^{2+}(aq)$

4. Balance each reaction and calculate the standard reduction potential for each. Be sure to include the physical state of each product and reactant.

   a. $Cu^+(aq) + Ag^+(aq) \rightarrow Cu^{2+}(aq) + Ag(s)$
   b. $Sn(s) + Fe^{3+}(aq) \rightarrow Sn^{2+}(aq) + Fe^{2+}(aq)$
   c. $Mg(s) + Br_2(l) \rightarrow 2Br^-(aq) + Mg^{2+}(aq)$

5. Write a balanced chemical equation for each redox reaction.

   a. $H_2PO_2^-(aq) + SbO_2^-(aq) \rightarrow HPO_3^{2-}(aq) + Sb(s)$ in basic solution
   b. $HNO_2(aq) + I^-(aq) \rightarrow NO(g) + I_2(s)$ in acidic solution
   c. $N_2O(g) + ClO^-(aq) \rightarrow Cl^-(aq) + NO_2^-(aq)$ in basic solution
   d. $Br_2(l) \rightarrow Br^-(aq) + BrO_3^-(aq)$ in basic solution
   e. $Cl(CH_2)_2OH(aq) + K_2Cr_2O_7(aq) \rightarrow ClCH_2CO_2H(aq) + Cr^{3+}(aq)$ in acidic solution

6. Write a balanced chemical equation for each redox reaction.

   a. $I^-(aq) + HClO_2(aq) \rightarrow IO_3^-(aq) + Cl_2(g)$ in acidic solution
   b. $Cr^{2+}(aq) + O_2(g) \rightarrow Cr^{3+}(aq) + H_2O(l)$ in acidic solution
   c. $CrO_2^-(aq) + ClO^-(aq) \rightarrow CrO_4^{2-}(aq) + Cl^-(aq)$ in basic solution
   d. $S(s) + HNO_2(aq) \rightarrow H_2SO_3(aq) + N_2O(g)$ in acidic solution
   e. $F(CH_2)_2OH(aq) + K_2Cr_2O_7(aq) \rightarrow FCH_2CO_2H(aq) + Cr^{3+}(aq)$ in acidic solution

7. The standard cell potential for the oxidation of Pb to Pb^{2+} with the concomitant reduction of Cu^+ to Cu is 0.39 V. You know that E° for the Pb^{2+}/Pb couple is −0.13 V. What is E° for the Cu^+/Cu couple?

8. You have built a galvanic cell similar to the one in Figure 19.7 using an iron nail, a solution of $FeCl_2$, and an SHE. When the cell is connected, you notice that the iron nail begins to corrode. What else do you observe? Under standard conditions, what is E_{cell}?

9. Carbon is used to reduce iron ore to metallic iron. The overall reaction is as follows:

$$2Fe_2O_3 \bullet xH_2O(s) + 3C(s) \rightarrow 4Fe(l) + 3CO_2(g) + 2xH_2O(g)$$

Write the two half-reactions for this overall reaction.

10. Will each reaction occur spontaneously under standard conditions?

    a. $Cu(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$
    b. $Zn^{2+}(aq) + Pb(s) \rightarrow Zn(s) + Pb^{2+}(aq)$

11. Each reaction takes place in acidic solution. Balance each reaction and then determine whether it occurs spontaneously as written under standard conditions.

    a. $Se(s) + Br_2(l) \rightarrow H_2SeO_3(aq) + Br^-(aq)$
    b. $NO_3^-(aq) + S(s) \rightarrow HNO_2(aq) + H_2SO_3(aq)$
    c. $Fe^{3+}(aq) + Cr^{3+}(aq) \rightarrow Fe^{2+}(aq) + Cr_2O_7^{2-}(aq)$

12. Calculate $E°_{cell}$ and $\Delta G°$ for the redox reaction represented by the cell diagram $Pt(s)|Cl_2(g, 1\ atm)||ZnCl_2(aq, 1\ M)|Zn(s)$. Will this reaction occur spontaneously?

13. If you place Zn-coated (galvanized) tacks in a glass and add an aqueous solution of iodine, the brown color of the iodine solution fades to a pale yellow. What has happened? Write the two half-reactions and the overall balanced chemical equation for this reaction. What is $E°_{cell}$?

14. Your lab partner wants to recover solid silver from silver chloride by using a 1.0 M solution of HCl and 1 atm H_2 under standard conditions. Will this plan work?

Numerical Answers

1. $Pt(s)|H_2(g, 1\ atm)\ |\ H^+(aq, 1M)||Cu^{2+}(aq)|Cu(s)$
3.

    a. $Cl_2(g) + H_2(g) \rightarrow 2Cl^-(aq) + 2H^+(aq)$; $E° = 1.358\ V$
    b. $Br_2(l) + 2Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$; $E° = 0.316\ V$
    c. $2Fe^{3+}(aq) + Cd(s) \rightarrow 2Fe^{2+}(aq) + Cd^{2+}(aq)$; $E° = 1.174\ V$

Conceptual Problems

1. The order of electrode potentials cannot always be predicted by ionization potentials and electron affinities. Why? Do you expect sodium metal to have a higher or a lower electrode potential than predicted from its ionization potential? What is its approximate electrode potential?
2. Without referring to tabulated data, of Br_2/Br^-, Ca^{2+}/Ca, O_2/OH^-, and Al^{3+}/Al, which would you expect to have the least negative electrode potential and which the most negative? Why?
3. Because of the sulfur-containing amino acids present in egg whites, eating eggs with a silver fork will tarnish the fork. As a chemist, you have all kinds of interesting cleaning products in your cabinet, including a 1 M solution of oxalic acid ($H_2C_2O_4$). Would you choose this solution to clean the fork that you have tarnished from eating scrambled eggs?
4. The electrode potential for the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ is 0.34 V under standard conditions. Is the potential for the oxidation of 0.5 mol of Cu equal to −0.34/2 V? Explain your answer.
5. Refer to Table 19.2 to predict
    A. Which species—$Sn^{4+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—can oxidize $MnO_2(s)$ to MNO_4^- under standard conditions.
    B. Which species—$Sn^{4+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—is the strongest oxidizing agent in aqueous solution.

Conceptual Answer

3. No; E° = −0.691 V for $Ag_2S(s) + 2e^- \rightarrow Ag(s) + S^{2-}(aq)$, which is too negative for Ag_2S to be spontaneously reduced by oxalic acid [E° = 0.49 V for $2CO_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2C_2O_4(aq)$]

5.

A. $Ag^+(aq)$; $H_2O_2(aq)$
B. $H_2O_2(aq)$

20.3: Ecell, ΔG, and K

Conceptual Problems

1. State whether you agree or disagree with this reasoning and explain your answer: Standard electrode potentials arise from the number of electrons transferred. The greater the number of electrons transferred, the greater the measured potential difference. If 1 mol of a substance produces 0.76 V when 2 mol of electrons are transferred—as in $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$—then 0.5 mol of the substance will produce 0.76/2 V because only 1 mol of electrons is transferred.
2. What is the relationship between the measured cell potential and the total charge that passes through a cell? Which of these is dependent on concentration? Which is dependent on the identity of the oxidant or the reductant? Which is dependent on the number of electrons transferred?
3. In the equation $w_{max} = -nFE°_{cell}$, which quantities are extensive properties and which are intensive properties?
4. For any spontaneous redox reaction, E is positive. Use thermodynamic arguments to explain why this is true.
5. State whether you agree or disagree with this statement and explain your answer: Electrochemical methods are especially useful in determining the reversibility or irreversibility of reactions that take place in a cell.
6. Although the sum of two half-reactions gives another half-reaction, the sum of the potentials of the two half-reactions cannot be used to obtain the potential of the net half-reaction. Why? When does the sum of two half-reactions correspond to the overall reaction? Why?
7. Occasionally, you will find high-quality electronic equipment that has its electronic components plated in gold. What is the advantage of this?
8. Blood analyzers, which measure pH, P_{CO_2}, and P_{O_2}, are frequently used in clinical emergencies. For example, blood P_{CO_2} is measured with a pH electrode covered with a plastic membrane that is permeable to CO_2. Based on your knowledge of how electrodes function, explain how such an electrode might work. Hint: $CO_2(g) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$.
9. Concentration cells contain the same species in solution in two different compartments. Explain what produces a voltage in a concentration cell. When does V = 0 in such a cell?
10. Describe how an electrochemical cell can be used to measure the solubility of a sparingly soluble salt.

Conceptual Answers

3. extensive: w_{max} and n; intensive: $E°_{cell}$

7. Gold is highly resistant to corrosion because of its very positive reduction potential.

Numerical Problems

1. The chemical equation for the combustion of butane is as follows:

$$C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$$

This reaction has ΔH° = −2877 kJ/mol. Calculate $E°_{cell}$ and then determine ΔG°. Is this a spontaneous process? What is the change in entropy that accompanies this process at 298 K?

2. How many electrons are transferred during the reaction $Pb(s) + Hg_2Cl_2(s) \rightarrow PbCl_2(aq) + 2Hg(l)$? What is the standard cell

potential? Is the oxidation of Pb by Hg_2Cl_2 spontaneous? Calculate $\Delta G°$ for this reaction.

3. For the cell represented as $Al(s)|Al^{3+}(aq)||Sn^{2+}(aq), Sn^{4+}(aq)|Pt(s)$, how many electrons are transferred in the redox reaction? What is the standard cell potential? Is this a spontaneous process? What is $\Delta G°$?

4. Explain why the sum of the potentials for the half-reactions $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ and $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ does not equal the potential for the reaction $Sn^{4+}(aq) + 4e^- \rightarrow Sn(s)$. What is the net cell potential? Compare the values of $\Delta G°$ for the sum of the potentials and the actual net cell potential.

5. Based on Table 19.2 and Chapter 29, do you agree with the proposed potentials for the following half-reactions? Why or why not?

   a. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, $E° = 0.68$ V
   b. $Ce^{4+}(aq) + 4e^- \rightarrow Ce(s)$, $E° = -0.62$ V

6. For each reaction, calculate $E°_{cell}$ and then determine $\Delta G°$. Indicate whether each reaction is spontaneous.

   a. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
   b. $K_2S_2O_6(aq) + I_2(s) \rightarrow 2KI(aq) + 2K_2SO_4(aq)$
   c. $Sn(s) + CuSO_4(aq) \rightarrow Cu(s) + SnSO_4(aq)$

7. What is the standard change in free energy for the reaction between Ca^{2+} and Na(s) to give Ca(s) and Na^+? Do the sign and magnitude of $\Delta G°$ agree with what you would expect based on the positions of these elements in the periodic table? Why or why not?

8. In acidic solution, permanganate (MnO_4^-) oxidizes Cl^- to chlorine gas, and MnO_4^- is reduced to $Mn^{2+}(aq)$.

   a. Write the balanced chemical equation for this reaction.
   b. Determine $E°_{cell}$.
   c. Calculate the equilibrium constant.

9. Potentiometric titrations are an efficient method for determining the endpoint of a redox titration. In such a titration, the potential of the solution is monitored as measured volumes of an oxidant or a reductant are added. Data for a typical titration, the potentiometric titration of Fe(II) with a 0.1 M solution of Ce(IV), are given in the following table. The starting potential has been arbitrarily set equal to zero because it is the change in potential with the addition of the oxidant that is important.

Titrant (mL)	E (mV)
2.00	50
6.00	100
9.00	255
10.00	960
11.00	1325
12.00	1625
14.00	1875

   a. Write the balanced chemical equation for the oxidation of Fe^{2+} by Ce^{4+}.
   b. Plot the data and then locate the endpoint.
   c. How many millimoles of Fe^{2+} did the solution being titrated originally contain?

10. The standard electrode potential (E°) for the half-reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ is −0.257 V. What pH is needed for this reaction to take place in the presence of 1.00 atm $H_2(g)$ as the reductant if $[Ni^{2+}]$ is 1.00 M?

11. The reduction of Mn(VII) to Mn(s) by $H_2(g)$ proceeds in five steps that can be readily followed by changes in the color of the solution. Here is the redox chemistry:

    a. $MnO_4–(aq) + e^- \rightarrow MnO_4^{2-}(aq)$; E° = +0.56 V (purple → dark green)
    b. $MnO_4^{2-}(aq) + 2e^- + 4H^+(aq) \rightarrow MnO_2(s)$; E° = +2.26 V (dark green → dark brown solid)
    c. $MnO_2(s) + e^- + 4H^+(aq) \rightarrow Mn^{3+}(aq)$; E° = +0.95 V (dark brown solid → red-violet)
    d. $Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; E° = +1.51 V (red-violet → pale pink)
    e. $Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$; E° = –1.18 V (pale pink → colorless)

    a. Is the reduction of MnO_4^- to $Mn^{3+}(aq)$ by $H_2(g)$ spontaneous under standard conditions? What is E°cell?
    b. Is the reduction of $Mn^{3+}(aq)$ to Mn(s) by $H_2(g)$ spontaneous under standard conditions? What is E°cell?

12. Mn(III) can disproportionate (both oxidize and reduce itself) by means of the following half-reactions:

$$Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)\ E°=1.51\ V$$
$$Mn^{3+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 4H^+(aq) + e^-\ E°=0.95\ V$$

    a. What is E° for the disproportionation reaction?
    b. Is disproportionation more or less thermodynamically favored at low pH than at pH 7.0? Explain your answer.
    c. How could you prevent the disproportionation reaction from occurring?

13. For the reduction of oxygen to water, E° = 1.23 V. What is the potential for this half-reaction at pH 7.00? What is the potential in a 0.85 M solution of NaOH?

14. The biological molecule abbreviated as NADH (reduced nicotinamide adenine dinucleotide) can be formed by reduction of NAD^+ (nicotinamide adenine dinucleotide) via the half-reaction $NAD^+ + H^+ + 2e^- \rightarrow NADH$; E° = –0.32 V.

    a. Would NADH be able to reduce acetate to pyruvate?
    b. Would NADH be able to reduce pyruvate to lactate?
    c. What potential is needed to convert acetate to lactate?

$$acetate + CO_2 + 2H^+ + 2e^- \rightarrow pyruvate + H_2O\ E° = –0.70\ V$$
$$pyruvate + 2H^+ + 2e^- \rightarrow lactate\ E° = –0.185\ V$$

15. Given the following biologically relevant half-reactions, will FAD (flavin adenine dinucleotide), a molecule used to transfer electrons whose reduced form is $FADH_2$, be an effective oxidant for the conversion of acetaldehyde to acetate at pH 4.00?

$$acetate + 2H^+ + 2e^- \rightarrow acetaldehyde + H_2O\ E° = –0.58\ V$$
$$FAD + 2H^+ + 2e^- \rightarrow FADH_2\ E° = –0.18\ V$$

16. Ideally, any half-reaction with E° > 1.23 V will oxidize water as a result of the half-reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.

    a. Will FeO_42^- oxidize water if the half-reaction for the reduction of Fe(VI) → Fe(III) is $FeO_4^{2-}(aq) + 8H^+(aq) + 3e^- \rightarrow Fe^{3+}(aq) + 4H_2O$; E° = 1.9 V?
    b. What is the highest pH at which this reaction will proceed spontaneously if $[Fe^{3+}] = [FeO_4^{2-}]$ = 1.0 M and P_{O_2}= 1.0 atm?

17. Under acidic conditions, ideally any half-reaction with E° > 1.23 V will oxidize water via the reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.

    a. Will aqueous acidic $KMnO_4$ evolve oxygen with the formation of MnO_2?
    b. At pH 14.00, what is E° for the oxidation of water by aqueous $KMnO_4$ (1 M) with the formation of MnO_2?
    c. At pH 14.00, will water be oxidized if you are trying to form MnO_2 from MnO_4^{2-} via the reaction $2MnO_4^{2-}(aq) + 2H_2O(l)$

$\rightarrow 2MnO_2(s) + O_2(g) + 4OH^-(aq)$?

18. Complexing agents can bind to metals and result in the net stabilization of the complexed species. What is the net thermodynamic stabilization energy that results from using CN^- as a complexing agent for Mn^{3+}/Mn^{2+}?

$$Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)\ E° = 1.51\ V$$
$$Mn(CN)_6^{3-}(aq) + e^- \rightarrow Mn(CN)_6^{4-}\ E° = -0.24\ V$$

19. You have constructed a cell with zinc and lead amalgam electrodes described by the cell diagram $Zn(Hg)(s)|Zn(NO_3)_2(aq)||Pb(NO_3)_2(aq)|Pb(Hg)(s)$. If you vary the concentration of $Zn(NO_3)_2$ and measure the potential at different concentrations, you obtain the following data:

$Zn(NO_3)_2$ (M)	E_{cell} (V)
0.0005	0.7398
0.002	0.7221
0.01	0.7014

    a. Write the half-reactions that occur in this cell.
    b. What is the overall redox reaction?
    c. What is $E°_{cell}$? What is $\Delta G°$ for the overall reaction?
    d. What is the equilibrium constant for this redox reaction?

20. Hydrogen gas reduces Ni^{2+} according to the following reaction: $Ni^{2+}(aq) + H_2(g) \rightarrow Ni(s) + 2H^+(aq)$; $E°_{cell} = -0.25$ V; $\Delta H = 54$ kJ/mol.
    a. What is K for this redox reaction?
    b. Is this reaction likely to occur?
    c. What conditions can be changed to increase the likelihood that the reaction will occur as written?
    d. Is the reaction more likely to occur at higher or lower pH?

21. The silver–silver bromide electrode has a standard potential of 0.07133 V. What is K_{sp} of AgBr?

Numerical Answers

3. $6e^-$; $E°_{cell} = 1.813$ V; the reaction is spontaneous; $\Delta G° = -525$ kJ/mol Al.

13. yes; $E° = 0.40$ V

17. a. yes; $E° = 0.45$ V
    b. 0.194 V
    c. yes; $E° = 0.20$ V

20.4: Ecell as a Function of Concentrations

Conceptual Problems

1. What advantage is there to using an alkaline battery rather than a Leclanché dry cell?
2. Why does the density of the fluid in lead–acid batteries drop when the battery is discharged?
3. What type of battery would you use for each application and why?

    a. powering an electric motor scooter
    b. a backup battery for a smartphone
    c. powering an iPod

4. Why are galvanic cells used as batteries and fuel cells? What is the difference between a battery and a fuel cell? What is the advantage to using highly concentrated or solid reactants in a battery?

Conceptual Answer

3.

a. lead storage battery
b. lithium–iodine battery
c. NiCad, NiMH, or lithium ion battery (rechargeable)

Numerical Problem

1. This reaction is characteristic of a lead storage battery:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

If you have a battery with an electrolyte that has a density of 1.15 g/cm^3 and contains 30.0% sulfuric acid by mass, is the potential greater than or less than that of the standard cell?

Numerica Answer

1. $[H_2SO_4]$ = 3.52 M; E > E°

20.5: Batteries: Producing Electricity Through Chemical Reactions

20.6: Corrosion: Unwanted Voltaic Cells

20.7: Electrolysis: Causing Nonspontaneous Reactions to Occur

Conceptual Problems

1. Why might an electrochemical reaction that is thermodynamically favored require an overvoltage to occur?
2. How could you use an electrolytic cell to make quantitative comparisons of the strengths of various oxidants and reductants?
3. Why are mixtures of molten salts, rather than a pure salt, generally used during electrolysis?
4. Two solutions, one containing $Fe(NO_3)_2{\cdot}6H_2O$ and the other containing the same molar concentration of $Fe(NO_3)_3{\cdot}6H_2O$, were electrolyzed under identical conditions. Which solution produced the most metal? Justify your answer.

Numerical Problems

1. The electrolysis of molten salts is frequently used in industry to obtain pure metals. How many grams of metal are deposited from these salts for each mole of electrons?
   a. $AlCl_3$
   b. $MgCl_2$
   c. $FeCl_3$

2. Electrolysis is the most direct way of recovering a metal from its ores. However, the $Na^+(aq)/Na(s)$, $Mg^{2+}(aq)/Mg(s)$, and $Al^{3+}(aq)/Al(s)$ couples all have standard electrode potentials (E°) more negative than the reduction potential of water at pH 7.0 (−0.42 V), indicating that these metals can never be obtained by electrolysis of aqueous solutions of their salts. Why? What reaction would occur instead?

3. What volume of chlorine gas at standard temperature and pressure is evolved when a solution of $MgCl_2$ is electrolyzed using a current of 12.4 A for 1.0 h?

4. What mass of copper metal is deposited if a 5.12 A current is passed through a $Cu(NO_3)_2$ solution for 1.5 h.

5. What mass of PbO_2 is reduced when a current of 5.0 A is withdrawn over a period of 2.0 h from a lead storage battery?

6. Electrolysis of $Cr^{3+}(aq)$ produces $Cr^{2+}(aq)$. If you had 500 mL of a 0.15 M solution of $Cr^{3+}(aq)$, how long would it take to reduce the Cr^{3+} to Cr^{2+} using a 0.158 A current?

7. Predict the products obtained at each electrode when aqueous solutions of the following are electrolyzed.
   a. $AgNO_3$
   b. RbI

8. Predict the products obtained at each electrode when aqueous solutions of the following are electrolyzed.
   a. $MgBr_2$
   b. $Hg(CH_3CO_2)_2$
   c. $Al_2(SO_4)_3$

Answers

3. 5.2 L
7.
   a. cathode: Ag(s); anode: $O_2(g)$;
   b. cathode: $H_2(g)$; anode: $I_2(s)$

20.8: Industrial Electrolysis Processes

True or False:

1. The main product of the chlor-alkali process is NaCl.
2. A diaphragm cell yields the purest concentration of NaOH.
3. In a diaphragm cell, the oxidation of Cl^- ions occurs at the anode and the reduction of Na^+ occurs at the cathode.
4. H_2 gas is a byproduct of the chlor-alkali process.
5. Electrorefining for copper is effective because out of the all of the metals in an ore, only copper is oxidized at the anode at low voltages.
6. A mercury cell uses mercury liquid as the cathode.
7. The chlor-alkali process is spontaneous.
8. A mercury cell requires a higher voltage and more energy than a diaphragm cell.
9. In a membrane cell, all ions can freely be exchanged between the membrane.
10. The reaction between NaOH and Cl_2 gas is necessary for the chlor-alkali process.

Outside Links

- Electrolysis: Industrial Uses (Wikipedia)
- Industrial Electrolysis and Electrochemical Engineering (electrochem.org pdf)
- Wagenknecht, John H. "Industrial organic electrosynthesis (SOA-Electrochemistry)." *J. Chem. Educ.* **1983**, *60*, 271.

Check Your Understanding: Answers

1. False - The chlor-alkali process is the electrolysis of NaCl, not the electrosynthesis. NaCl is one of the main **reactants** of the chlor-alkali process
2. False - A diaphragm cell yields the most impure NaOH. The mercury cell yields purer NaOH, followed by the membrane cell with the purest.
3. False - Due to the high voltage required to reduce Na ions (meaning the large negative standard electrode reduction potential of sodium), the reduction of water occurs instead.
4. True - Yes, H_2 gas is produced at the cathode while Cl_2 gas is produced at the anode.

5. False - Though Au, Ag and Pt are not oxidized, Sb, Bi and Sn are oxidized but are precipitated as they form hydroxides and oxides. Fe, Ni, Co and Zn are oxidized as well, but they are dissolved in water. Thus, even though copper is the only pure metal solid we have left, other impurities are oxidized as well.
6. True - Liquid mercury at the bottom of the tank acts as the cathode. More mercury is constantly cycled back into the tank as amalgam is treated with water.
7. False - Electrosynthesis requires energy.
8. True - A mercury cell needs 3400 kWh/ton Cl_2 opposed to 2500 in a diaphragm cell.
9. False - In a membrane cell, only cations can pass through the membrane into the cathode. This explains why the NaOH on the cathode side has so little chlorine ion impurities.
10. False - If Cl_2 and NaOH come into contact, Cl_2 turns into ClO^-, ClO_3^-, Cl ions. This is not desirable, so the difference in solution levels is used to prevent backflow of NaOH into the anode side.

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21: CHEMISTRY OF THE MAIN-GROUP ELEMENTS I

Petrucci: *General Chemistry*
Principles and Modern Applications

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21.1: Periodic Trends and Charge Density

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 21.1.1. 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 21.1.1 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.

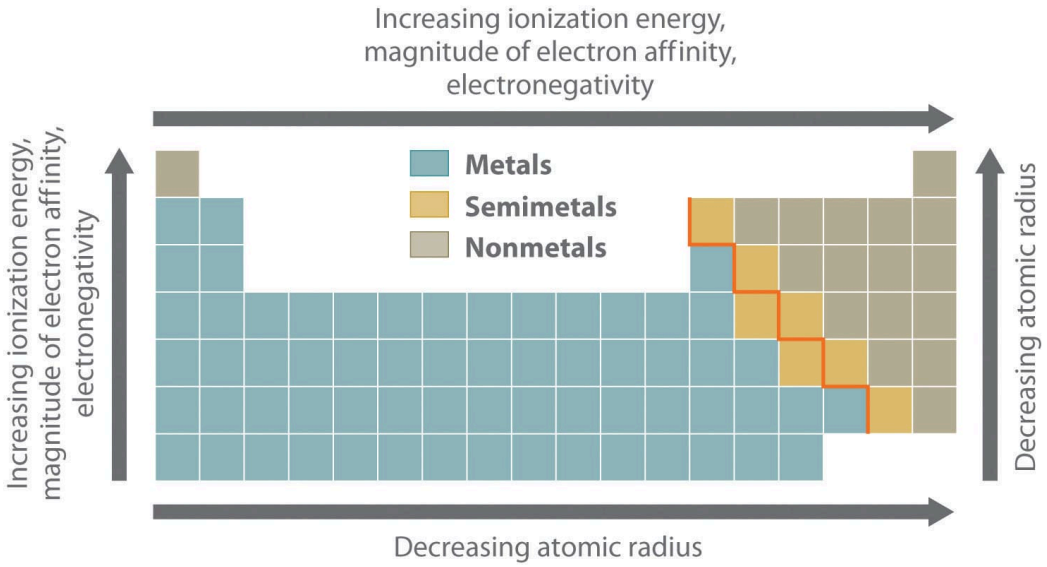


Figure 21.1.1: Summary of Periodic Trends in Atomic Properties. *Ionization energies, the magnitude of electron affinities, and electronegativities generally increase from left to right and from bottom to top. In contrast, atomic size decreases from left to right and from bottom to top. Consequently, 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.

Note

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.

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.

Note

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 21.1.1 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 21.1.1: 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 21.1.1, 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 21.1.1

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 21.1.1

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 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.

Key Takeaway

- 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.

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21.2: Group 1: The Alkali Metals

Learning Objectives

1. To describe how the alkali metals are isolated.
2. To be familiar with the reactions, compounds, and complexes of the alkali metals.

The alkali metals are so reactive that they are never found in nature in elemental form. Although some of their ores are abundant, isolating them from their ores is somewhat difficult. For these reasons, the group 1 elements were unknown until the early 19th century, when Sir Humphry Davy first prepared sodium (Na) and potassium (K) by passing an electric current through molten alkalis. (The ashes produced by the combustion of wood are largely composed of potassium and sodium carbonate.) Lithium (Li) was discovered 10 years later when the Swedish chemist Johan Arfwedson was studying the composition of a new Brazilian mineral. Cesium (Cs) and rubidium (Rb) were not discovered until the 1860s, when Robert Bunsen conducted a systematic search for new elements. Known to chemistry students as the inventor of the Bunsen burner, Bunsen's spectroscopic studies of ores showed sky blue and deep red emission lines that he attributed to two new elements, Cs and Rb, respectively. Francium (Fr) is found in only trace amounts in nature, so our knowledge of its chemistry is limited. All the isotopes of Fr have very short half-lives, in contrast to the other elements in group 1.

Humphry Davy (1778–1829)

Davy was born in Penzance, Cornwall, England. He was a bit of a wild man in the laboratory, often smelling and tasting the products of his experiments, which almost certainly shortened his life. He discovered the physiological effects that cause nitrous oxide to be called "laughing gas" (and became addicted to it!), and he almost lost his eyesight in an explosion of nitrogen trichloride (NCl_3), which he was the first to prepare. Davy was one of the first to recognize the utility of Alessandro Volta's "electric piles" (batteries). By connecting several "piles" in series and inserting electrodes into molten salts of the alkali metals and alkaline earth metals, he was able to isolate six previously unknown elements as pure metals: sodium, potassium, calcium, strontium, barium, and magnesium. He also discovered boron and was the first to prepare phosphine (PH_3) and hydrogen telluride (H_2Te), both of which are highly toxic.

Robert Wilhelm Bunsen (1811–1899)

Bunsen was born and educated in Göttingen, Germany. His early work dealt with organic arsenic compounds, whose highly toxic nature and explosive tendencies almost killed him and did cost him an eye. He designed the Bunsen burner, a reliable gas burner, and used it and emission spectra to discover cesium (named for its blue line) and rubidium (named for its red line).

Preparation of the Alkali Metals

Because the alkali metals are among the most potent reductants known, obtaining them in pure form requires a considerable input of energy. Pure lithium and sodium for example, are typically prepared by the electrolytic reduction of molten chlorides:

$$\mathrm{LiCl(l)} \rightarrow \mathrm{Li(l)} + \frac{1}{2}\mathrm{Cl_2(g)} \tag{21.2.1}$$

In practice, $CaCl_2$ is mixed with LiCl to lower the melting point of the lithium salt. The electrolysis is carried out in an argon atmosphere rather than the nitrogen atmosphere typically used for substances that are highly reactive with O_2 and water because Li reacts with nitrogen gas to form lithium nitride (Li_3N). Metallic sodium is produced by the electrolysis of a molten mixture of NaCl and $CaCl_2$. In contrast, potassium is produced commercially from the reduction of KCl by Na, followed by the fractional distillation of K(g). Although rubidium and cesium can also be produced by electrolysis, they are usually obtained by reacting their hydroxide salts with a reductant such as Mg:

$$2RbOH_{(s)} + Mg_{(s)} \rightarrow 2Rb_{(l)} + Mg(OH)_{2(s)} \tag{21.2.2}$$

Massive deposits of essentially pure NaCl and KCl are found in nature and are the major sources of sodium and potassium. The other alkali metals are found in low concentrations in a wide variety of minerals, but ores that contain high concentrations of these elements are relatively rare. No concentrated sources of rubidium are known, for example, even though it is the 16th most abundant element on Earth. Rubidium is obtained commercially by isolating the 2%–4% of Rb present as an impurity in micas, minerals that are composed of sheets of complex hydrated potassium–aluminum silicates.

Alkali metals are recovered from silicate ores in a multistep process that takes advantage of the pH-dependent solubility of selected salts of each metal ion. The steps in this process are leaching, which uses sulfuric acid to dissolve the desired alkali metal ion and Al^{3+} from the ore; basic precipitation to remove Al^{3+} from the mixture as $Al(OH)_3$; selective precipitation of the insoluble alkali metal carbonate; dissolution of the salt again in hydrochloric acid; and isolation of the metal by evaporation and electrolysis. Figure 21.2.1 illustrates the isolation of liquid lithium from a lithium silicate ore by this process.

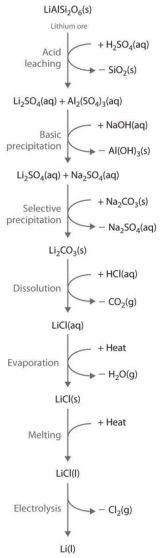


Figure 21.2.1: Isolating Lithium from Spodumene, a Lithium Silicate Ore. *The key steps are acid leaching, basic precipitation of aluminum hydroxide, selective precipitation of insoluble lithium carbonate, conversion to lithium chloride, evaporation, and electrolysis. The other alkali metals and the alkaline earth metals are recovered from their ores by similar processes.*

General Properties of the Alkali Metals

Various properties of the group 1 elements are summarized in Table 21.2.1. In keeping with overall periodic trends, the atomic and ionic radii increase smoothly from Li to Cs, and the first ionization energies decrease as the atoms become larger. As a result of their low first ionization energies, the alkali metals have an overwhelming tendency to form ionic compounds where they have a +1 charge. All the alkali metals have relatively high electron affinities because the addition of an electron produces an anion (M^-) with an ns^2 electron configuration. The densities of the elements generally increase from Li to Cs, reflecting another common trend: because the atomic masses of the elements increase more rapidly than the atomic volumes as you go down a group, the densest elements are near the bottom of the periodic table. An unusual trend in the group 1 elements is the smooth decrease in the melting and boiling points from Li to Cs. As a result, Cs (melting point = 28.5°C) is one of only three metals (the others are Ga and Hg) that are liquids at body temperature (37°C).

Table 21.2.1: Selected Properties of the Group 1 Elements

	Lithium	Sodium	Potassium	Rubidium	Cesium	Francium
atomic symbol	Li	Na	K	Rb	Cs	Fr
atomic number	3	11	19	37	55	87
***The values cited are for four-coordinate ions except for Rb^+ and Cs^+, whose values are given for the six-coordinate ion.**						

	Lithium	Sodium	Potassium	Rubidium	Cesium	Francium
atomic mass	6.94	22.99	39.10	85.47	132.91	223
valence electron configuration	$2s^1$	$3s^1$	$4s^1$	$5s^1$	$6s^1$	$7s^1$
melting point/ boiling point (°C)	180.5/1342	97.8/883	63.5/759	39.3/688	28.5/671	27/—
density (g/cm^3) at 25°C	0.534	0.97	0.89	1.53	1.93	—
atomic radius (pm)	167	190	243	265	298	—
first ionization energy (kJ/mol)	520	496	419	403	376	393
most common oxidation state	+1	+1	+1	+1	+1	+1
ionic radius (pm)*	76	102	138	152	167	—
electron affinity (kJ/mol)	−60	−53	−48	−47	−46	—
electronegativity	1.0	0.9	0.8	0.8	0.8	0.7
standard electrode potential (E°, V)	−3.04	−2.71	−2.93	−2.98	−3.03	—
product of reaction with O_2	Li_2O	Na_2O_2	KO_2	RbO_2	CsO_2	—
type of oxide	basic	basic	basic	basic	basic	—
product of reaction with N_2	Li_3N	none	none	none	none	—
product of reaction with X_2	LiX	NaX	KX	RbX	CsX	—
product of reaction with H_2	LiH	NaH	KH	RbH	CsH	—
***The values cited are for four-coordinate ions except for Rb^+ and Cs^+, whose values are given for the six-coordinate ion.**						

The standard reduction potentials (E°) of the alkali metals do not follow the trend based on ionization energies. Unexpectedly, lithium is the strongest reductant, and sodium is the weakest (Table 21.2.1). Because Li^+ is much smaller than the other alkali metal cations, its hydration energy is the highest. The high hydration energy of Li^+ more than compensates for its higher ionization energy, making lithium metal the strongest reductant in aqueous solution. This apparent anomaly is an example of how the physical or the chemical behaviors of the elements in a group are often determined by the subtle interplay of opposing periodic trends.

Reactions and Compounds of the Alkali Metals

All alkali metals are electropositive elements with an ns^1 valence electron configuration, forming the monocation (M^+) by losing the single valence electron. Because removing a second electron would require breaking into the (n – 1) closed shell, which is energetically prohibitive, the chemistry of the alkali metals is largely that of ionic compounds that contain M^+ ions. However, as we discuss later, the lighter group 1 elements also form a series of organometallic compounds that contain polar covalent M–C

bonds.

All the alkali metals react vigorously with the halogens (group 17) to form the corresponding ionic halides, where X is a halogen:

$$2M_{(s)} + X_{2(s,l,g)} \rightarrow 2M^{+}X^{-}_{(s)} \tag{21.2.3}$$

Similarly, the alkali metals react with the heavier chalcogens (sulfur, selenium, and tellurium in group 16) to produce metal chalcogenides, where Y is S, Se, or Te:

$$2M_{(s)} + Y_{(s)} \rightarrow M_2Y_{(s)} \tag{21.2.4}$$

When excess chalcogen is used, however, a variety of products can be obtained that contain chains of chalcogen atoms, such as the sodium polysulfides (Na_2S_n, where n = 2–6). For example, Na_2S_3 contains the S_3^{2-} ion, which is V shaped with an S–S–S angle of about 103°. The one-electron oxidation product of the trisulfide ion (S_3^-) is responsible for the intense blue color of the gemstones lapis lazuli and blue ultramarine (Figure 21.2.2).

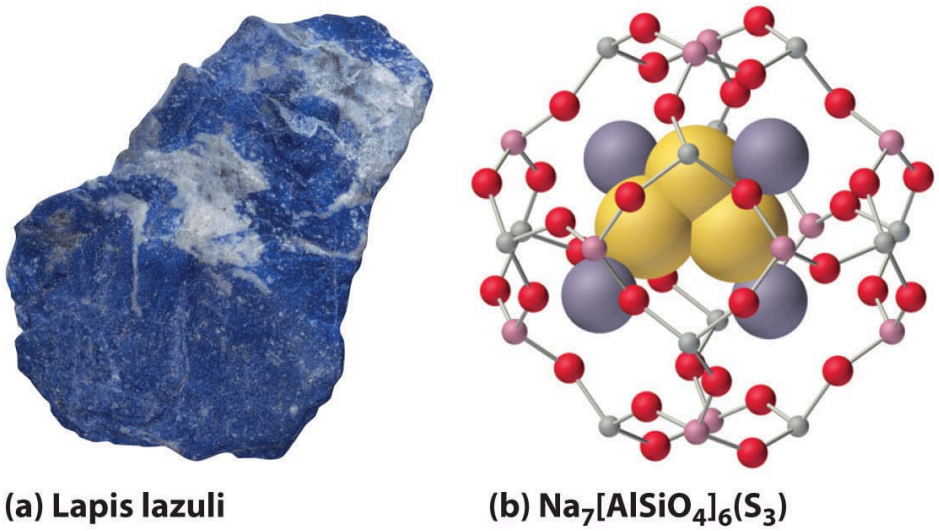


Figure 21.2.2: The Trisulfide Anion Is Responsible for the Deep Blue Color of Some Gemstones. *(a) The rich blue color of lapis lazuli is due to small amounts of the normally unstable S_3^- anion. (b) The aluminosilicate cages of the minerals (zeolites) that make up the matrix of blue ultramarine stabilize the reactive anion; excess Na^+ ions in the structure balance the negative charges on the zeolite framework and the S_3^- anion.*

Reacting the alkali metals with oxygen, the lightest element in group 16, is more complex, and the stoichiometry of the product depends on both the metal:oxygen ratio and the size of the metal atom. For instance, when alkali metals burn in air, the observed products are Li_2O (white), Na_2O_2 (pale yellow), KO_2 (orange), RbO_2 (brown), and CsO_2 (orange). Only Li_2O has the stoichiometry expected for a substance that contains two M^+ cations and one O^{2-} ion. In contrast, Na_2O_2 contains the O_2^{2-} (peroxide) anion plus two Na^+ cations. The other three salts, with stoichiometry MO_2, contain the M^+ cation and the O_2^- (superoxide) ion. Because O^{2-} is the smallest of the three oxygen anions, it forms a stable ionic lattice with the smallest alkali metal cation (Li^+). In contrast, the larger alkali metals—potassium, rubidium, and cesium—react with oxygen in air to give the metal superoxides. Because the Na^+ cation is intermediate in size, sodium reacts with oxygen to form a compound with an intermediate stoichiometry: sodium peroxide. Under specific reaction conditions, however, it is possible to prepare the oxide, peroxide, and superoxide salts of all five alkali metals, except for lithium superoxide (LiO_2).



A crystal of spodumene ($LiAlSi_2O_6$). This mineral is one of the most important lithium ores.

The chemistry of the alkali metals is largely that of ionic compounds containing the M^+ ions.

The alkali metal peroxides and superoxides are potent oxidants that react, often vigorously, with a wide variety of reducing agents, such as charcoal or aluminum metal. For example, Na_2O_2 is used industrially for bleaching paper, wood pulp, and fabrics such as linen and cotton. In submarines, Na_2O_2 and KO_2 are used to purify and regenerate the air by removing the CO_2 produced by respiration and replacing it with O_2. Both compounds react with CO_2 in a redox reaction in which O_2^{2-} or O_2^- is simultaneously oxidized and reduced, producing the metal carbonate and O_2:

$$2Na_2O_{2(s)} + 2CO_{2(g)} \rightarrow 2Na_2CO_{3(s)} + O_{2(g)} \tag{21.2.5}$$

$$4KO_{2(s)} + 2CO_{2(g)} \rightarrow 2K_2CO_{3(s)} + 3O_{2(g)} \tag{21.2.6}$$

The presence of water vapor, the other product of respiration, makes KO_2 even more effective at removing CO_2 because potassium bicarbonate, rather than potassium carbonate, is formed:

$$4KO_{2(s)} + 4CO_{2(g)} + 2H_2O_{(g)} \rightarrow 4KHCO_{3(s)} + 3O_{2(g)} \tag{21.2.7}$$

Notice that 4 mol of CO_2 are removed in this reaction, rather than 2 mol in Equation 21.10.

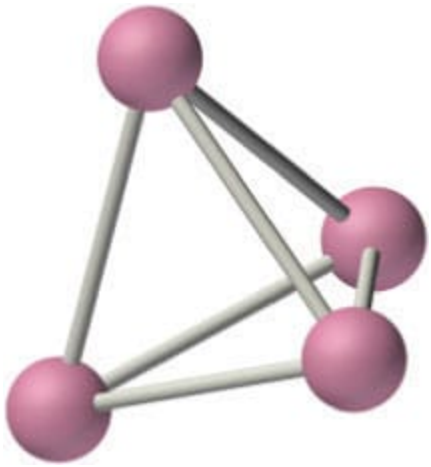
Lithium, the lightest alkali metal, is the only one that reacts with atmospheric nitrogen, forming lithium nitride (Li_3N). Lattice energies again explain why the larger alkali metals such as potassium do not form nitrides: packing three large K^+ cations around a single relatively small anion is energetically unfavorable. In contrast, all the alkali metals react with the larger group 15 elements phosphorus and arsenic to form metal phosphides and arsenides (where Z is P or As):

$$12M_{(s)} + Z_{4(s)} \rightarrow 4M_3Z_{(s)} \tag{21.2.8}$$

Because of lattice energies, only lithium forms a stable oxide and nitride.

The alkali metals react with all group 14 elements, but the compositions and properties of the products vary significantly. For example, reaction with the heavier group 14 elements gives materials that contain polyatomic anions and three-dimensional cage structures, such as K_4Si_4 whose structure is shown here. In contrast, lithium and sodium are oxidized by carbon to produce a compound with the stoichiometry M_2C_2 (where M is Li or Na):

$$2M_{(s)} + 2C_{(s)} \rightarrow M_2C_{2(s)} \tag{21.2.9}$$



The three-dimensional cage structure of the Si_4^{4-} ion in the ionic compound K_4S_4. The Si_4^{4-} ion is isoelectronic and isostructural with the P_4 molecule.

The same compounds can be obtained by reacting the metal with acetylene (C_2H_2). In this reaction, the metal is again oxidized, and hydrogen is reduced:

$$2M_{(s)} + C_2H_{2(g)} \rightarrow M_2C_{2(s)} + H_{2(g)} \tag{21.2.10}$$

The acetylide ion (C_2^{2-}), formally derived from acetylene by the loss of both hydrogens as protons, is a very strong base. Reacting acetylide salts with water produces acetylene and MOH(aq).

The heavier alkali metals (K, Rb, and Cs) also react with carbon in the form of graphite. Instead of disrupting the hexagonal sheets of carbon atoms, however, the metals insert themselves between the sheets of carbon atoms to give new substances called **graphite intercalation compounds** (part (a) in Figure 21.2.3). The stoichiometries of these compounds include MC_{60} and MC_{48}, which are black/gray; MC_{36} and MC_{24}, which are blue; and MC_8, which is bronze (part (b) in Figure 21.2.3). The remarkably high electrical conductivity of these compounds (about 200 times greater than graphite) is attributed to a net transfer of the valence electron of the alkali metal to the graphite layers to produce, for example, $K^+C_8^-$.

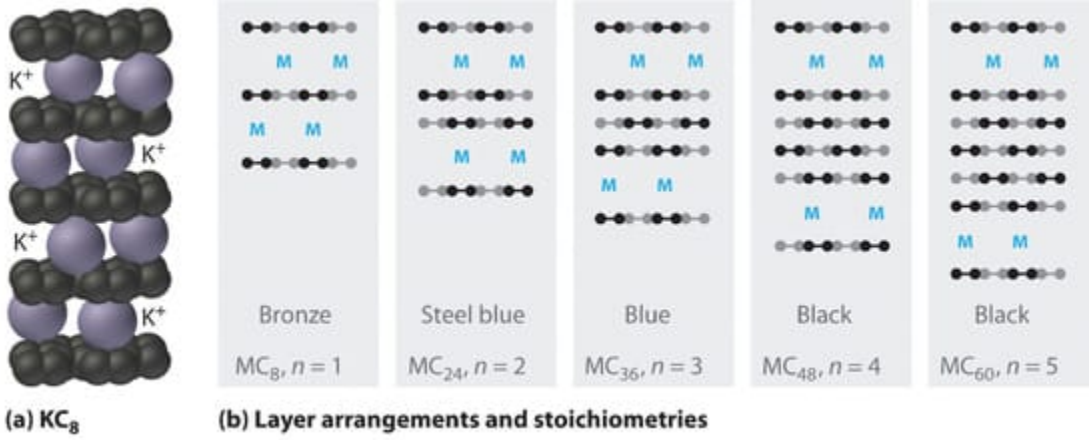


Figure 21.2.3 Graphite Intercalation Compounds. Reacting graphite with alkali metals such as K, Rb, and Cs results in partial reduction of the graphite and insertion of layers of alkali metal cations between sets of n layers of carbon atoms. (a) In KC_8, layers of K^+ ions are inserted between every pair of carbon layers, giving n = 1. (b) The stoichiometry and color of intercalation compounds depend on the number of layers of carbon atoms (n) between each layer of intercalated metal atoms. This schematic diagram illustrates the most common structures that have been observed.

All the alkali metals react directly with gaseous hydrogen at elevated temperatures to produce ionic hydrides (M^+H^-):

$$2M_{(s)} + H_{2(g)} \rightarrow 2MH_{(s)} \tag{21.2.11}$$

All are also capable of reducing water to produce hydrogen gas:

$$\mathrm{M(s) + H_2O(l) \rightarrow \frac{1}{2}H_2(g) + MOH(aq)} \tag{21.2.12}$$

Although lithium reacts rather slowly with water, sodium reacts quite vigorously (Figure 21.2.4), and the heavier alkali metals (K, Rb, and Cs) react so vigorously that they invariably explode. This trend, which is not consistent with the relative magnitudes of the reduction potentials of the elements, serves as another example of the complex interplay of different forces and phenomena—in this case, kinetics and thermodynamics. Although the driving force for the reaction is greatest for lithium, the heavier metals have lower melting points. The heat liberated by the reaction causes them to melt, and the larger surface area of the liquid metal in contact with water greatly accelerates the reaction rate.

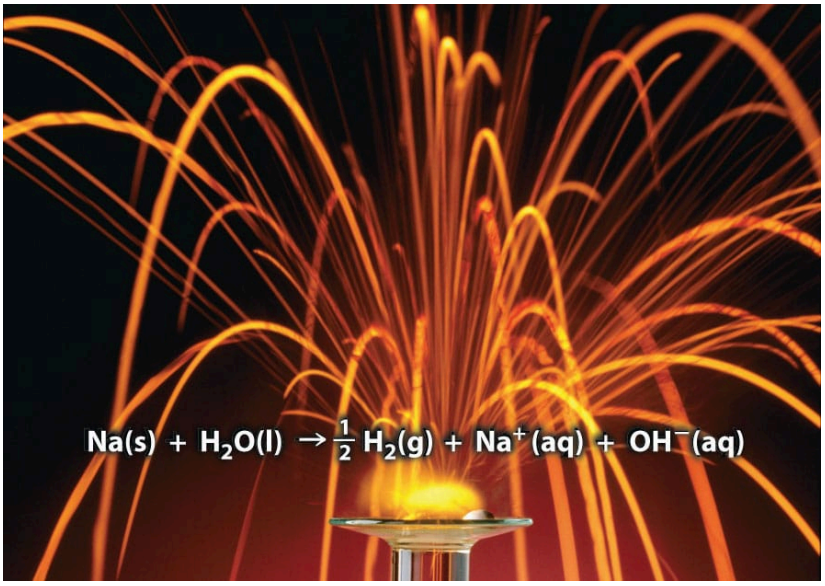


Figure 21.2.4: Reacting Sodium with Water. Like most elements in groups 1 and 2, sodium reacts violently with water. The products are the Na^+(aq) ion and hydrogen gas, which is potentially explosive when mixed with air.

Alkali metal cations are found in a wide variety of ionic compounds. In general, any alkali metal salt can be prepared by reacting the alkali metal hydroxide with an acid and then evaporating the water:

$$2MOH_{(aq)} + H_2SO_{4(aq)} \rightarrow M_2SO_{4(aq)} + 2H_2O_{(l)} \tag{21.2.13}$$

$$MOH_{(aq)} + HNO_{3(aq)} \rightarrow MNO_{3(aq)} + H_2O_{(l)} \tag{21.2.14}$$

Hydroxides of alkali metals also can react with organic compounds that contain an acidic hydrogen to produce a salt. An example is the preparation of sodium acetate (CH_3CO_2Na) by reacting sodium hydroxide and acetic acid:

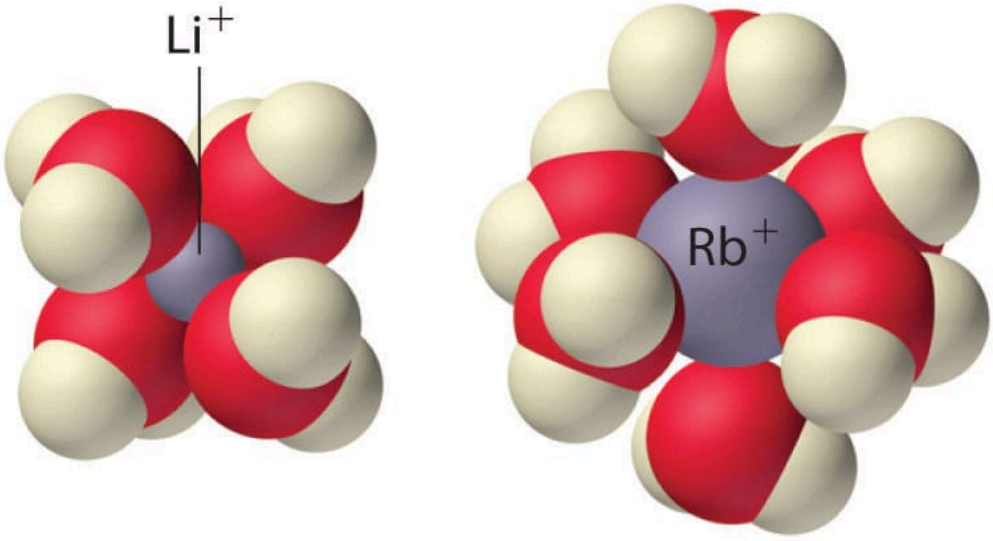
$$CH_3CO_2H_{(aq)} + NaOH_{(s)} \rightarrow CH_3CO_2Na_{(aq)} + H_2O_{(l)} \tag{21.2.15}$$

Soap is a mixture of the sodium and potassium salts of naturally occurring carboxylic acids, such as palmitic acid [$CH_3(CH_2)_{14}CO_2H$] and stearic acid [$CH_3(CH_2)_{16}CO_2H$]. Lithium salts, such as lithium stearate [$CH_3(CH_2)_{14}CO_2Li$], are used as additives in motor oils and greases.

Complexes of the Alkali Metals

Because of their low positive charge (+1) and relatively large ionic radii, alkali metal cations have only a weak tendency to react with simple Lewis bases to form metal complexes. Complex formation is most significant for the smallest cation (Li^+) and decreases with increasing radius. In aqueous solution, for example, Li^+ forms the tetrahedral $[Li(H_2O)_4]^+$ complex. In contrast, the larger alkali metal cations form octahedral $[M(H_2O)_6]^+$ complexes. Complex formation is primarily due to the electrostatic interaction of the metal cation with polar water molecules. Because of their high affinity for water, anhydrous salts that contain Li^+ and Na^+ ions (such as Na_2SO_4) are often used as drying agents. These compounds absorb trace amounts of water from

nonaqueous solutions to form hydrated salts, which are then easily removed from the solution by filtration.



The tetrahedral $[Li(H_2O)_4]^+$ and octahedral $[Rb(H_2O)_6]^+$ complexes. The Li^+ ion is so small that it can accommodate only four water molecules around it, but the larger alkali metal cations tend to bind six water molecules.

> Because of their low positive charge (+1) and relatively large ionic radii, alkali metal cations have only a weak tendency to form complexes with simple Lewis bases.

Electrostatic interactions also allow alkali metal ions to form complexes with certain cyclic polyethers and related compounds, such as crown ethers and cryptands. As discussed in Chapter 13, **crown ethers** are cyclic polyethers that contain four or more oxygen atoms separated by two or three carbon atoms. All crown ethers have a central cavity that can accommodate a metal ion coordinated to the ring of oxygen atoms, and crown ethers with rings of different sizes prefer to bind metal ions that fit into the cavity. For example, 14-crown-4, with the smallest cavity that can accommodate a metal ion, has the highest affinity for Li^+, whereas 18-crown-6 forms the strongest complexes with K^+.

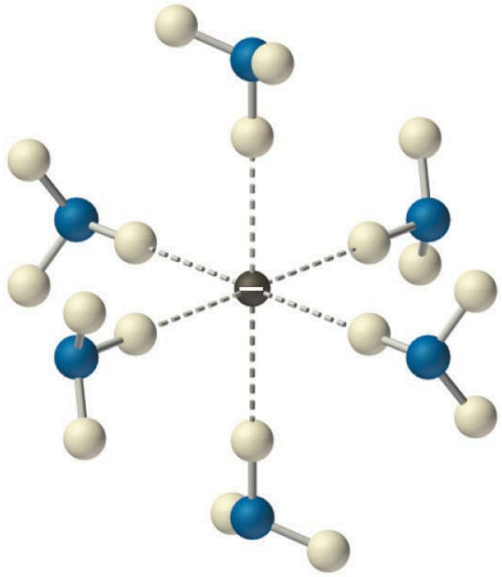
Cryptands are more nearly spherical analogues of crown ethers and are even more powerful and selective complexing agents. Cryptands consist of three chains containing oxygen that are connected by two nitrogen atoms (part (b) in Figure 13.7). They can completely surround (encapsulate) a metal ion of the appropriate size, coordinating to the metal by a lone pair of electrons on each O atom and the two N atoms. Like crown ethers, cryptands with different cavity sizes are highly selective for metal ions of particular sizes. Crown ethers and cryptands are often used to dissolve simple inorganic salts such as $KMnO_4$ in nonpolar organic solvents.

Liquid Ammonia Solutions

A remarkable feature of the alkali metals is their ability to dissolve reversibly in liquid ammonia. Just as in their reactions with water, reacting alkali metals with liquid ammonia eventually produces hydrogen gas and the metal salt of the conjugate base of the solvent—in this case, the amide ion (NH_2^-) rather than hydroxide:

$$\mathrm{M(s) + NH_3(l) \rightarrow \frac{1}{2}H_2(g) + M^+(am) + NH_2^-(am)} \tag{21.2.16}$$

where the (am) designation refers to an ammonia solution, analogous to (aq) used to indicate aqueous solutions. Without a catalyst, the reaction in Equation 21.20 tends to be rather slow. In many cases, the alkali metal amide salt (MNH_2) is not very soluble in liquid ammonia and precipitates, but when dissolved, very concentrated solutions of the alkali metal are produced. One mole of Cs metal, for example, will dissolve in as little as 53 mL (40 g) of liquid ammonia. The pure metal is easily recovered when the ammonia evaporates.



Solvated electrons. The presence of solvated electrons (e^-, NH_3) in solutions of alkali metals in liquid ammonia is indicated by the intense color of the solution and its electrical conductivity.

Solutions of alkali metals in liquid ammonia are intensely colored and good conductors of electricity due to the presence of solvated electrons (e^-, NH_3), which are not attached to single atoms. A solvated electron is loosely associated with a cavity in the ammonia solvent that is stabilized by hydrogen bonds. Alkali metal–liquid ammonia solutions of about 3 M or less are deep blue (Figure 21.2.5) and conduct electricity about 10 times better than an aqueous NaCl solution because of the high mobility of the solvated electrons. As the concentration of the metal increases above 3 M, the color changes to metallic bronze or gold, and the conductivity increases to a value comparable with that of the pure liquid metals.

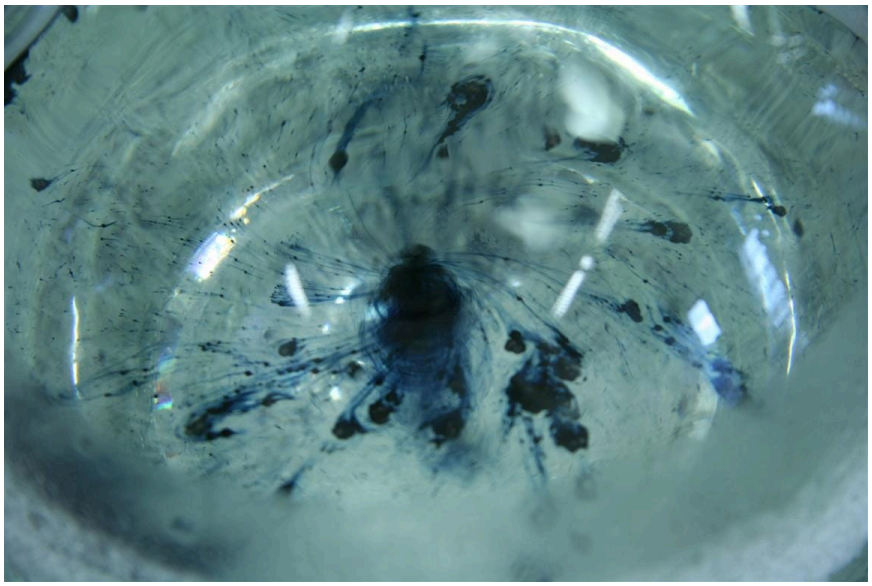


Figure 21.2.5: Alkali Metal–Liquid Ammonia Solutions. Most metals are insoluble in virtually all solvents, but the alkali metals (and the heavier alkaline earth metals) dissolve readily in liquid ammonia to form solvated metal cations and solvated electrons, which give the solution a deep blue color. Image copyrighted by the Klein research group.

In addition to solvated electrons, solutions of alkali metals in liquid ammonia contain the metal cation (M^+), the neutral metal atom (M), metal dimers (M_2), and the metal anion (M^-). The anion is formed by adding an electron to the singly occupied ns valence orbital of the metal atom. Even in the absence of a catalyst, these solutions are not very stable and eventually decompose to the thermodynamically favored products: $M^+NH_2^-$ and hydrogen gas (Equation 21.20). Nonetheless, the solvated electron is a potent reductant that is often used in synthetic chemistry.

Organometallic Compounds of the Group 1 Elements

Compounds that contain a metal covalently bonded to a carbon atom of an organic species are called **organometallic compounds**. The properties and reactivities of organometallic compounds differ greatly from those of either the metallic or organic components. Because of its small size, lithium, for example, forms an extensive series of covalent organolithium compounds, such as methyllithium ($LiCH_3$), which are by far the most stable and best-known group 1 organometallic compounds. These volatile, low-melting-point solids or liquids can be sublimed or distilled at relatively low temperatures and are soluble in nonpolar solvents. Like organic compounds, the molten solids do not conduct electricity to any significant degree. Organolithium compounds have a tendency to form oligomers with the formula $(RLi)_n$, where R represents the organic component. For example, in both the solid state and solution, methyllithium exists as a tetramer with the structure shown in Figure 21.2.6, where each triangular face of the Li_4 tetrahedron is bridged by the carbon atom of a methyl group. Effectively, the carbon atom of each CH_3 group is using a single pair of electrons in an sp^3 hybrid lobe to bridge three lithium atoms, making this an example of two-electron, four-center bonding. Clearly, such a structure, in which each carbon atom is apparently bonded to six other atoms, cannot be explained using any of the electron-pair bonding schemes. Molecular orbital theory can explain the bonding in methyllithium, but the description is beyond the scope of this text.

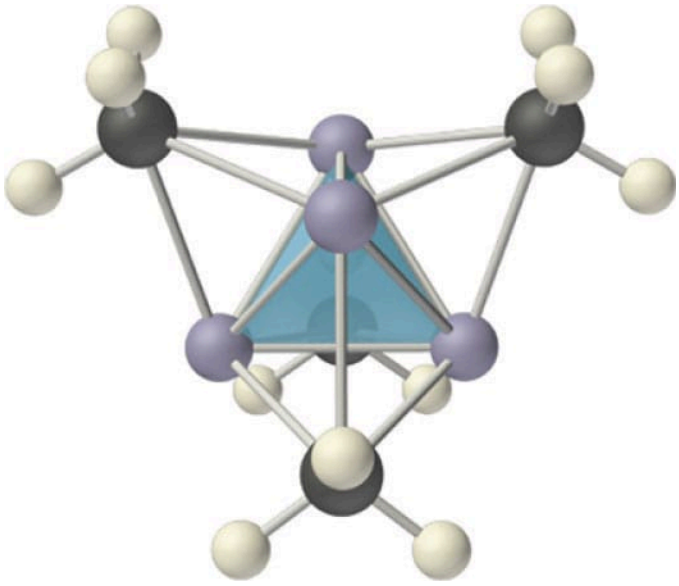


Figure 21.2.6: The Tetrameric Structure of Methyllithium. m*Methyllithium is not an ionic compound; it exists as tetrameric $(CH_3Li)_4$ molecules. The structure consists of a tetrahedral arrangement of four lithium atoms, with the carbon atom of a methyl group located above the middle of each triangular face of the tetrahedron. The carbon atoms thus bridge three lithium atoms to form four-center, two-electron bonds.*

- The properties and reactivities of organometallic compounds differ greatly from those of either the metallic or organic components.
- Organosodium and organopotassium compounds are more ionic than organolithium compounds. They contain discrete M^+ and R^- ions and are insoluble or only sparingly soluble in nonpolar solvents.

Uses of the Alkali Metals

Because sodium remains liquid over a wide temperature range (97.8–883°C), it is used as a coolant in specialized high-temperature applications, such as nuclear reactors and the exhaust valves in high-performance sports car engines. Cesium, because of its low ionization energy, is used in photosensors in automatic doors, toilets, burglar alarms, and other electronic devices. In these devices, cesium is ionized by a beam of visible light, thereby producing a small electric current; blocking the light interrupts the electric current and triggers a response.

Compounds of sodium and potassium are produced on a huge scale in industry. Each year, the top 50 industrial compounds include NaOH, used in a wide variety of industrial processes; Na_2CO_3, used in the manufacture of glass; K_2O, used in porcelain glazes; and Na_4SiO_4, used in detergents.

Several other alkali metal compounds are also important. For example, Li_2CO_3 is one of the most effective treatments available for manic depression or bipolar disorder. It appears to modulate or dampen the effect on the brain of changes in the level of neurotransmitters, which are biochemical substances responsible for transmitting nerve impulses between neurons. Consequently, patients who take “lithium” do not exhibit the extreme mood swings that characterize this disorder.

21.2.1

For each application, choose the more appropriate substance based on the properties and reactivities of the alkali metals and their compounds. Explain your choice in each case.

a. For a reaction that requires a strong base in a solution of tetrahydrofuran (THF), would you use LiOH or CsOH?
b. To extinguish a fire caused by burning lithium metal, would you use water, CO_2, N_2 gas, or sand (SiO_2)?
c. Both $LiNO_3$and $CsNO_3$ are highly soluble in acetone (2-propanone). Which of these alkali metal salts would you use to precipitate I^- from an acetone solution?

Given: application and selected alkali metals

Asked for: appropriate metal for each application

Strategy:

Use the properties and reactivities discussed in this section to determine which alkali metal is most suitable for the indicated application.

Solution

a. Both LiOH and CsOH are ionic compounds that contain the hydroxide anion. Li^+, however, is much smaller than Cs^+, so the Li^+ cation will be more effectively solvated by the oxygen of THF with its lone pairs of electrons. This difference will have two effects: (1) LiOH is likely to be much more soluble than CsOH in the nonpolar solvent, which could be a significant advantage, and (2) the solvated Li^+ ions are less likely to form tight ion pairs with the OH^- ions in the relatively nonpolar solution, making the OH^- more basic and thus more reactive. Thus LiOH is the better choice.
b. Lithium is a potent reductant that reacts with water to form LiOH and H_2 gas, so adding a source of hydrogen such as water to a lithium fire is likely to produce an explosion. Lithium also reacts with oxygen and nitrogen in the air to form Li_2O and Li_3N, respectively, so we would not expect nitrogen to extinguish a lithium fire. Because CO_2 is a gaseous molecule that contains carbon in its highest accessible oxidation state (+4), adding CO_2 to a strong reductant such as Li should result in a vigorous redox reaction. Thus water, N_2, and CO_2 are all unsuitable choices for extinguishing a lithium fire. In contrast, sand is primarily SiO_2, which is a network solid that is not readily reduced. Smothering a lithium fire with sand is therefore the best choice.
c. The salt with the smaller cation has the higher lattice energy, and high lattice energies tend to decrease the solubility of a salt. However, the solvation energy of the cation is also important in determining solubility, and small cations tend to have higher solvation energies. Recall that high solvation energies tend to increase the solubility of ionic substances. Thus CsI should be the least soluble of the alkali metal iodides, and LiI the most soluble. Consequently, $CsNO_3$ is the better choice.

21.2.1

Indicate which of the alternative alkali metals or their compounds given is more appropriate for each application.

a. drying agent for an organic solvent—Li_2SO_4 or Rb_2SO_4
b. removing trace amounts of N_2 from highly purified Ar gas—Li, K, or Cs
c. reacting with an alkyl halide (formula RX) to prepare an organometallic compound (formula MR)—Li or K

Answer

a. Li_2SO_4
b. Li
c. Li

21.2.2

Predict the products of each reaction and then balance each chemical equation.

a. $Na(s) + O_2(g) \rightarrow$
b. $Li_2O(s) + H_2O(l) \rightarrow$
c. $K(s) + CH_3OH(l) \rightarrow$
d. $Li(s) + CH_3Cl(l) \rightarrow$
e. $Li_3N(s) + KCl(s) \rightarrow$

Given: reactants

Asked for: products and balanced chemical equation

Strategy:

A Determine whether one of the reactants is an oxidant or a reductant or a strong acid or a strong base. If so, a redox reaction or an acid–base reaction is likely to occur. Identify the products of the reaction.

B If a reaction is predicted to occur, balance the chemical equation.

Solution

a. **A** Sodium is a reductant, and oxygen is an oxidant, so a redox reaction is most likely. We expect an electron to be transferred from Na (thus forming Na^+) to O_2. We now need to determine whether the reduced product is a superoxide (O_2^-), peroxide (O_2^{2-}), or oxide (O^{2-}). Under normal reaction conditions, the product of the reaction of an alkali metal with oxygen depends on the identity of the metal. Because of differences in lattice energy, Li produces the oxide (Li_2O), the heavier metals (K, Rb, Cs) produce the superoxide (MO_2), and Na produces the peroxide (Na_2O_2).

B The balanced chemical equation is $2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$.

b. **A** Li_2O is an ionic salt that contains the oxide ion (O^{2-}), which is the completely deprotonated form of water and thus is expected to be a strong base. The other reactant, water, is both a weak acid and a weak base, so we can predict that an acid–base reaction will occur.

B The balanced chemical equation is $Li_2O(s) + H_2O(l) \rightarrow 2LiOH(aq)$.

c. **A** Potassium is a reductant, whereas methanol is both a weak acid and a weak base (similar to water). A weak acid produces H^+, which can act as an oxidant by accepting an electron to form $\frac{1}{2}H_2$. This reaction, therefore, is an acid dissociation that is driven to completion by a reduction of the protons as they are released.

B The balanced chemical equation is as follows: $\mathrm{K(s) + CH_3OH(l) \rightarrow \frac{1}{2}H_2(g) + CH_3OK(soln)}$.

d. **A** One of the reactants is an alkali metal, a potent reductant, and the other is an alkyl halide. Any compound that contains a carbon–halogen bond can, in principle, be reduced, releasing a halide ion and forming an organometallic compound. That outcome seems likely in this case because organolithium compounds are among the most stable organometallic compounds known.

B Two moles of lithium are required to balance the equation: $2Li(s) + CH_3Cl(l) \rightarrow LiCl(s) + CH_3Li(soln)$.

e. **A** Lithium nitride and potassium chloride are largely ionic compounds. The nitride ion (N^{3-}) is a very strong base because it is the fully deprotonated form of ammonia, a weak acid. An acid–base reaction requires an acid as well as a base, however, and KCl is not acidic. What about a redox reaction? Both substances contain ions that have closed-shell valence electron configurations. The nitride ion could act as a reductant by donating electrons to an oxidant and forming N_2. KCl is not an oxidant, however, and a redox reaction requires an oxidant as well as a reductant.

B We conclude that the two substances will not react with each other.

21.2.2

Predict the products of each reaction and balance each chemical equation.

a. $K(s) + N_2(g) \rightarrow$
b. $Li_3N(s) + H_2O(l) \rightarrow$
c. $Na(s) + (CH_3)_2NH(soln) \rightarrow$
d. $C_6H_5Li(soln) + D_2O(l) \rightarrow C_6H_5D(l) + LiOD(soln)$
e. $CH_3CH_2Cl(soln) + 2Li \rightarrow$

Answer

a. no reaction
b. $Li_3N(s) + 3H_2O(l) \rightarrow NH_3(aq) + 3LiOH(aq)$
c. $\mathrm{Na(s) + (CH_3)_2NH(soln) \rightarrow \frac{1}{2}H_2(g) + Na[(CH_3)_2N](soln)}$
d. $C_6H_5Li(soln) + D_2O(l) \rightarrow C_6H_5D(l) + LiOD(soln)$
e. $CH_3CH_2Cl(soln) + 2Li \rightarrow CH_3CH_2Li(soln) + LiCl(soln)$

Summary

The alkali metals are potent reductants whose chemistry is largely that of ionic compounds containing the M^+ ion. Alkali metals have only a weak tendency to form complexes with simple Lewis bases. The first alkali metals to be isolated (Na and K) were obtained by passing an electric current through molten potassium and sodium carbonates. The alkali metals are among the most potent reductants known; most can be isolated by electrolysis of their molten salts or, in the case of rubidium and cesium, by reacting their hydroxide salts with a reductant. They can also be recovered from their silicate ores using a multistep process. Lithium, the strongest reductant, and sodium, the weakest, are examples of the physical and chemical effects of opposing periodic trends. The alkali metals react with halogens (group 17) to form ionic halides; the heavier chalcogens (group 16) to produce metal chalcogenides; and oxygen to form compounds, whose stoichiometry depends on the size of the metal atom. The peroxides and superoxides are potent oxidants. The only alkali metal to react with atmospheric nitrogen is lithium. Heavier alkali metals react with graphite to form graphite intercalation compounds, substances in which metal atoms are inserted between the sheets of carbon atoms. With heavier group 14 elements, alkali metals react to give polyatomic anions with three-dimensional cage structures. All alkali metals react with hydrogen at high temperatures to produce the corresponding hydrides, and all reduce water to produce hydrogen gas. Alkali metal salts are prepared by reacting a metal hydroxide with an acid, followed by evaporation of the water. Both Li and Na salts are used as drying agents, compounds that are used to absorb water. Complexing agents such as crown ethers and cryptands can accommodate alkali metal ions of the appropriate size. Alkali metals can also react with liquid ammonia to form solutions that slowly decompose to give hydrogen gas and the metal salt of the amide ion (NH_2^-). These solutions, which contain unstable solvated electrons loosely associated with a cavity in the solvent, are intensely colored, good conductors of electricity, and excellent reductants. Alkali metals can react with organic compounds that contain an acidic proton to produce salts. They can also form organometallic compounds, which have properties that differ from those of their metallic and organic components.

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21.3: Group 2: The Alkaline Earth Metals

Learning Objectives

- To describe how to isolate the alkaline earth metals.
- To be familiar with the reactions, compounds, and complexes of the alkaline earth metals.

Like the alkali metals, the alkaline earth metals are so reactive that they are never found in elemental form in nature. Because they form +2 ions that have very negative reduction potentials, large amounts of energy are needed to isolate them from their ores. Four of the six group 2 elements—magnesium (Mg), calcium (Ca), strontium (Sr), and barium (Ba)—were first isolated in the early 19th century by Sir Humphry Davy, using a technique similar to the one he used to obtain the first alkali metals. In contrast to the alkali metals, however, compounds of the alkaline earth metals had been recognized as unique for many centuries. In fact, the name alkali comes from the Arabic al-qili, meaning “ashes,” which were known to neutralize acids. Medieval alchemists found that a portion of the ashes would melt on heating, and these substances were later identified as the carbonates of sodium and potassium (M_2CO_3). The ashes that did not melt (but did dissolve in acid), originally called alkaline earths, were subsequently identified as the alkaline earth oxides (MO). In 1808, Davy was able to obtain pure samples of Mg, Ca, Sr, and Ba by electrolysis of their chlorides or oxides.

Beryllium (Be), the lightest alkaline earth metal, was first obtained in 1828 by Friedrich Wöhler in Germany and simultaneously by Antoine Bussy in France. The method used by both men was reduction of the chloride by the potent “new” reductant, potassium:

$$\mathrm{BeCl_2(s) + 2K(s) \xrightarrow{\Delta} Be(s) + 2KCl(s)} \tag{21.3.1}$$

Radium was discovered in 1898 by Pierre and Marie Curie, who processed tons of residue from uranium mines to obtain about 120 mg of almost pure $RaCl_2$. Marie Curie was awarded the Nobel Prize in Chemistry in 1911 for its discovery. Because of its low abundance and high radioactivity however, radium has few uses.

Preparation of the Alkaline Earth Metals

The alkaline earth metals are produced for industrial use by electrolytic reduction of their molten chlorides, as indicated in this equation for calcium:

$$CaCl_{2\ (l)} \rightarrow Ca_{(l)} + Cl_{2\ (g)} \tag{21.3.2}$$

The group 2 metal chlorides are obtained from a variety of sources. For example, $BeCl_2$ is produced by reacting HCl with beryllia (BeO), which is obtained from the semiprecious stone beryl $[Be_3Al_2(SiO_3)_6]$.



A crystal of beryl. Beryl is a gemstone and an important source of beryllium.

Chemical reductants can also be used to obtain the group 2 elements. For example, magnesium is produced on a large scale by heating a form of limestone called dolomite ($CaCO_3{\cdot}MgCO_3$) with an inexpensive iron/silicon alloy at 1150°C. Initially CO_2 is

released, leaving behind a mixture of CaO and MgO; Mg^{2+} is then reduced:

$$2CaO \cdot MgO_{(s)} + Fe/Si_{(s)} \rightarrow 2Mg(l) + Ca_2SiO_{4\ (s)} + Fe(s) \tag{21.3.3}$$

An early source of magnesium was an ore called magnesite ($MgCO_3$) from the district of northern Greece called Magnesia. Strontium was obtained from strontianite ($SrCO_3$) found in a lead mine in the town of Strontian in Scotland. The alkaline earth metals are somewhat easier to isolate from their ores, as compared to the alkali metals, because their carbonate and some sulfate and hydroxide salts are insoluble.



A crystal of strontianite. Both strontianite, one of the most important strontium ores, and strontium are named after the town of Strontian, Scotland, the location of one of the first mines for strontium ores.

General Properties of the Alkaline Earth Metals

Several important properties of the alkaline earth metals are summarized in Table 21.3.1. Although many of these properties are similar to those of the alkali metals (Table 21.3.1), certain key differences are attributable to the differences in the valence electron configurations of the two groups (ns^2 for the alkaline earth metals versus ns^1 for the alkali metals).

Table 21.3.1: Selected Properties of the Group 2 Elements

	Beryllium	Magnesium	Calcium	Strontium	Barium	Radium
atomic symbol	Be	Mg	Ca	Sr	Ba	Ra
atomic number	4	12	20	38	56	88
atomic mass	9.01	24.31	40.08	87.62	137.33	226
valence electron configuration	$2s^2$	$3s^2$	$4s^2$	$5s^2$	$6s^2$	$7s^2$
melting point/ boiling point (°C)	1287/2471	650/1090	842/1484	777/1382	727/1897	700/—
density (g/cm^3) at 25°C	1.85	1.74	1.54	2.64	3.62	~5
atomic radius (pm)	112	145	194	219	253	—
***The values cited are for six-coordinate ions except for Be^{2+}, for which the value for the four-coordinate ion is given.**						

	Beryllium	Magnesium	Calcium	Strontium	Barium	Radium
first ionization energy (kJ/mol)	900	738	590	549	503	—
most common oxidation state	+2	+2	+2	+2	+2	+2
ionic radius (pm)*	45	72	100	118	135	—
electron affinity (kJ/mol)	≥ 0	≥ 0	−2	−5	−14	—
electronegativity	1.6	1.3	1.0	1.0	0.9	0.9
standard electrode potential (E°, V)	−1.85	−2.37	−2.87	−2.90	−2.91	−2.8
product of reaction with O_2	BeO	MgO	CaO	SrO	BaO_2	—
type of oxide	amphoteric	weakly basic	basic	basic	basic	—
product of reaction with N_2	none	Mg_3N_2	Ca_3N_2	Sr_3N_2	Ba_3N_2	—
product of reaction with X_2	BeX_2	MgX_2	CaX_2	SrX_2	BaX_2	—
product of reaction with H_2	none	MgH_2	CaH_2	SrH_2	BaH_2	—
***The values cited are for six-coordinate ions except for Be^{2+}, for which the value for the four-coordinate ion is given.**						

As with the alkali metals, the atomic and ionic radii of the alkaline earth metals increase smoothly from Be to Ba, and the ionization energies decrease. As we would expect, the first ionization energy of an alkaline earth metal, with an ns^2 valence electron configuration, is always significantly greater than that of the alkali metal immediately preceding it. The group 2 elements do exhibit some anomalies, however. For example, the density of Ca is less than that of Be and Mg, the two lightest members of the group, and Mg has the lowest melting and boiling points. In contrast to the alkali metals, the heaviest alkaline earth metal (Ba) is the strongest reductant, and the lightest (Be) is the weakest. The standard electrode potentials of Ca and Sr are not very different from that of Ba, indicating that the opposing trends in ionization energies and hydration energies are of roughly equal importance.

One major difference between the group 1 and group 2 elements is their electron affinities. With their half-filled ns orbitals, the alkali metals have a significant affinity for an additional electron. In contrast, the alkaline earth metals generally have little or no tendency to accept an additional electron because their ns valence orbitals are already full; an added electron would have to occupy one of the vacant np orbitals, which are much higher in energy.

Reactions and Compounds of the Alkaline Earth Metals

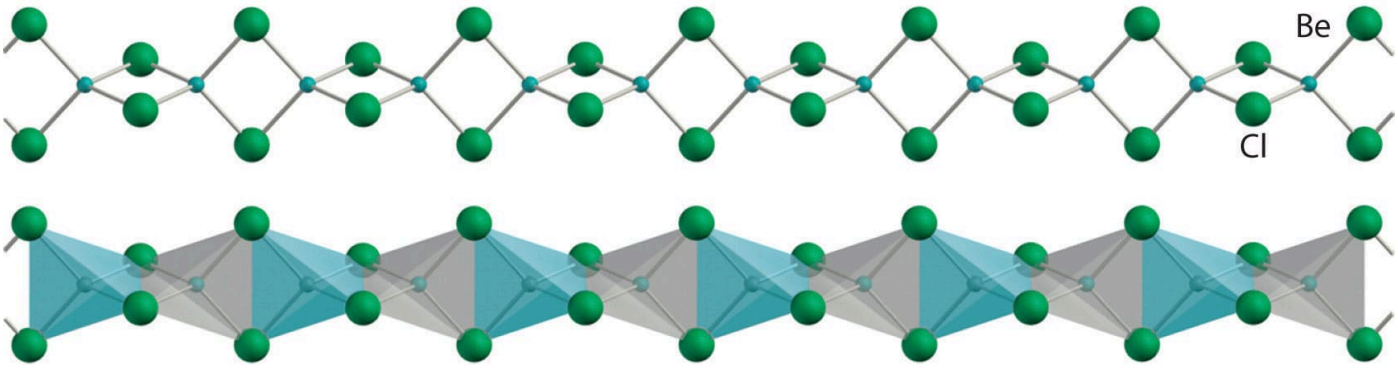
With their low first and second ionization energies, the group 2 elements almost exclusively form ionic compounds that contain M^{2+} ions. As expected, however, the lightest element (Be), with its higher ionization energy and small size, forms compounds that are largely covalent. Some compounds of Mg^{2+} also have significant covalent character. Hence organometallic compounds like those discussed for Li in group 1 are also important for Be and Mg in group 2.

> The group 2 elements almost exclusively form ionic compounds containing M^{2+} ions.

All alkaline earth metals react vigorously with the halogens (group 17) to form the corresponding halides (MX_2). Except for the beryllium halides, these compounds are all primarily ionic in nature, containing the M^{2+} cation and two X^- anions. The beryllium

halides, with properties more typical of covalent compounds, have a polymeric halide-bridged structure in the solid state, as shown for $BeCl_2$. These compounds are volatile, producing vapors that contain the linear X–Be–X molecules predicted by the valence-shell electron-pair repulsion (VSEPR) model. As expected for compounds with only four valence electrons around the central atom, the beryllium halides are potent Lewis acids. They react readily with Lewis bases, such as ethers, to form tetrahedral adducts in which the central beryllium is surrounded by an octet of electrons:

$$BeCl_{2(s)} + 2(CH_3CH_2)_2O_{(l)} \rightarrow BeCl_2[O(CH_2CH_3)_2]_{2(soln)} \tag{21.3.4}$$



Solid beryllium chloride ($BeCl_2$). The solid has a polymeric, halide-bridged structure.

Because of their higher ionization energy and small size, both Be and Mg form organometallic compounds.

The reactions of the alkaline earth metals with oxygen are less complex than those of the alkali metals. All group 2 elements except barium react directly with oxygen to form the simple oxide MO. Barium forms barium peroxide (BaO_2) because the larger O_2^{2-} ion is better able to separate the large Ba^{2+} ions in the crystal lattice. In practice, only BeO is prepared by direct reaction with oxygen, and this reaction requires finely divided Be and high temperatures because Be is relatively inert. The other alkaline earth oxides are usually prepared by the thermal decomposition of carbonate salts:

$$\mathrm{MCO_3(s) \xrightarrow{\Delta} MO(s) + CO_2(g)} \tag{21.3.5}$$

The reactions of the alkaline earth metals with the heavier chalcogens (Y) are similar to those of the alkali metals. When the reactants are present in a 1:1 ratio, the binary chalcogenides (MY) are formed; at lower M:Y ratios, salts containing polychalcogenide ions (Y_n^{2-}) are formed.

In the reverse of Equation 21.3.5, the oxides of Ca, Sr, and Ba react with CO_2 to regenerate the carbonate. Except for BeO, which has significant covalent character and is therefore amphoteric, all the alkaline earth oxides are basic. Thus they react with water to form the hydroxides—$M(OH)_2$:

$$MO_{(s)} + H_2O_{(l)} \rightarrow M^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{21.3.6}$$

and they dissolve in aqueous acid. Hydroxides of the lighter alkaline earth metals are insoluble in water, but their solubility increases as the atomic number of the metal increases. Because BeO and MgO are much more inert than the other group 2 oxides, they are used as refractory materials in applications involving high temperatures and mechanical stress. For example, MgO (melting point = 2825°C) is used to coat the heating elements in electric ranges.

The carbonates of the alkaline earth metals also react with aqueous acid to give CO_2 and H_2O:

$$MCO_{3(s)} + 2H^+_{(aq)} \rightarrow M^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)} \tag{21.3.7}$$

The reaction in Equation 21.3.7 is the basis of antacids that contain MCO_3, which is used to neutralize excess stomach acid.

The trend in the reactivities of the alkaline earth metals with nitrogen is the opposite of that observed for the alkali metals. Only the lightest element (Be) does not react readily with N_2 to form the nitride (M_3N_2), although finely divided Be will react at high temperatures. The higher lattice energy due to the highly charged M^{2+} and N^{3-} ions is apparently sufficient to overcome the chemical inertness of the N_2 molecule, with its N≡N bond. Similarly, all the alkaline earth metals react with the heavier group 15

elements to form binary compounds such as phosphides and arsenides with the general formula M_3Z_2.

> Higher lattice energies cause the alkaline earth metals to be more reactive than the alkali metals toward group 15 elements.

When heated, all alkaline earth metals, except for beryllium, react directly with carbon to form ionic carbides with the general formula MC_2. The most important alkaline earth carbide is calcium carbide (CaC_2), which reacts readily with water to produce acetylene. For many years, this reaction was the primary source of acetylene for welding and lamps on miners' helmets. In contrast, beryllium reacts with elemental carbon to form Be_2C, which formally contains the C^{4-} ion (although the compound is covalent). Consistent with this formulation, reaction of Be_2C with water or aqueous acid produces methane:

$$Be_2C_{(s)} + 4H_2O_{(l)} \rightarrow 2Be(OH)_{2(s)} + CH_{4(g)} \tag{21.3.8}$$

Beryllium does not react with hydrogen except at high temperatures (1500°C), although BeH_2 can be prepared at lower temperatures by an indirect route. All the heavier alkaline earth metals (Mg through Ba) react directly with hydrogen to produce the binary hydrides (MH_2). The hydrides of the heavier alkaline earth metals are ionic, but both BeH_2 and MgH_2 have polymeric structures that reflect significant covalent character. All alkaline earth hydrides are good reducing agents that react rapidly with water or aqueous acid to produce hydrogen gas:

$$CaH_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + 2H_{2(g)} \tag{21.3.9}$$

Like the alkali metals, the heavier alkaline earth metals are sufficiently electropositive to dissolve in liquid ammonia. In this case, however, two solvated electrons are formed per metal atom, and no equilibriums involving metal dimers or metal anions are known. Also, like the alkali metals, the alkaline earth metals form a wide variety of simple ionic salts with oxoanions, such as carbonate, sulfate, and nitrate. The nitrate salts tend to be soluble, but the carbonates and sulfates of the heavier alkaline earth metals are quite insoluble because of the higher lattice energy due to the doubly charged cation and anion. The solubility of the carbonates and the sulfates decreases rapidly down the group because hydration energies decrease with increasing cation size.

> The solubility of alkaline earth carbonate and sulfates decrease down the group because the hydration energies decrease.

Complexes of the Alkaline Earth Metals

Because of their higher positive charge (+2) and smaller ionic radii, the alkaline earth metals have a much greater tendency to form complexes with Lewis bases than do the alkali metals. This tendency is most important for the lightest cation (Be^{2+}) and decreases rapidly with the increasing radius of the metal ion.

> The alkaline earth metals have a substantially greater tendency to form complexes with Lewis bases than do the alkali metals.

The chemistry of Be^{2+} is dominated by its behavior as a Lewis acid, forming complexes with Lewis bases that produce an octet of electrons around beryllium. For example, Be^{2+} salts dissolve in water to form acidic solutions that contain the tetrahedral $[Be(H_2O)_4]^{2+}$ ion. Because of its high charge-to-radius ratio, the Be^{2+} ion polarizes coordinated water molecules, thereby increasing their acidity:

$$[Be(H_2O)_4]^{2+}_{(aq)} \rightarrow [Be(H_2O)_3(OH)]^{+}_{(aq)} + H^{+}_{(aq)} \tag{21.3.10}$$

Similarly, in the presence of a strong base, beryllium and its salts form the tetrahedral hydroxo complex: $[Be(OH)_4]^{2-}$. Hence beryllium oxide is amphoteric. Beryllium also forms a very stable tetrahedral fluoride complex: $[BeF_4]^{2-}$. Recall that beryllium halides behave like Lewis acids by forming adducts with Lewis bases (Equation 21.3.4).

The heavier alkaline earth metals also form complexes, but usually with a coordination number of 6 or higher. Complex formation is most important for the smaller cations (Mg^{2+} and Ca^{2+}). Thus aqueous solutions of Mg^{2+} contain the octahedral $[Mg(H_2O)_6]^{2+}$ ion. Like the alkali metals, the alkaline earth metals form complexes with neutral cyclic ligands like the crown ethers and cryptands discussed in Section 21.3.

Organometallic Compounds Containing Group 2 Elements

Like the alkali metals, the lightest alkaline earth metals (Be and Mg) form the most covalent-like bonds with carbon, and they form the most stable organometallic compounds. Organometallic compounds of magnesium with the formula RMgX, where R is an alkyl or aryl group and X is a halogen, are universally called Grignard reagents, after Victor Grignard (1871–1935), the French chemist who discovered them. Grignard reagents can be used to synthesize various organic compounds, such as alcohols, aldehydes, ketones, carboxylic acids, esters, thiols, and amines.

Uses of the Alkaline Earth Metals

Elemental magnesium is the only alkaline earth metal that is produced on a large scale (about 5×10^5 tn per year). Its low density (1.74 g/cm^3 compared with 7.87 g/cm^3 for iron and 2.70 g/cm^3 for aluminum) makes it an important component of the lightweight metal alloys used in aircraft frames and aircraft and automobile engine parts (Figure 21.3.1). Most commercial aluminum actually contains about 5% magnesium to improve its corrosion resistance and mechanical properties. Elemental magnesium also serves as an inexpensive and powerful reductant for the production of a number of metals, including titanium, zirconium, uranium, and even beryllium, as shown in the following equation:

$$TiCl_{4\ (l)} + 2Mg(s) \rightarrow Ti_{(s)} + 2MgCl_{2\ (s)} \tag{21.3.11}$$

The only other alkaline earth that is widely used as the metal is beryllium, which is extremely toxic. Ingestion of beryllium or exposure to beryllium-containing dust causes a syndrome called berylliosis, characterized by severe inflammation of the respiratory tract or other tissues. A small percentage of beryllium dramatically increases the strength of copper or nickel alloys, which are used in nonmagnetic, nonsparking tools (such as wrenches and screwdrivers), camera springs, and electrical contacts. The low atomic number of beryllium gives it a very low tendency to absorb x-rays and makes it uniquely suited for applications involving radioactivity. Both elemental Be and BeO, which is a high-temperature ceramic, are used in nuclear reactors, and the windows on all x-ray tubes and sources are made of beryllium foil.



Figure 21.3.1: Magnesium Alloys Are Lightweight and Corrosion Resistant. Because magnesium is about five times lighter than steel and 50% lighter than aluminum, it was long considered the “material of the future,” as shown in this 1950 concept Buick LeSabre sports car made almost entirely of magnesium and aluminum alloys. Modern aluminum alloys usually contain about 5% magnesium to improve their corrosion resistance and mechanical properties.

Millions of tons of calcium compounds are used every year. As discussed in earlier chapters, $CaCl_2$ is used as “road salt” to lower the freezing point of water on roads in cold temperatures. In addition, $CaCO_3$ is a major component of cement and an ingredient in many commercial antacids. “Quicklime” (CaO), produced by heating $CaCO_3$ (Equation 21.3.5), is used in the steel industry to remove oxide impurities, make many kinds of glass, and neutralize acidic soil. Other applications of group 2 compounds described in earlier chapters include the medical use of $BaSO_4$ in “barium milkshakes” for identifying digestive problems by x-rays and the use of various alkaline earth compounds to produce the brilliant colors seen in fireworks.

Example 21.3.1

For each application, choose the most appropriate substance based on the properties and reactivities of the alkaline earth metals and their compounds. Explain your choice in each case. Use any tables you need in making your decision, such as K_{sp} values (Table 17.1), lattice energies (Table 8.1), and band-gap energies.

a. To neutralize excess stomach acid that causes indigestion, would you use $BeCO_3$, $CaCO_3$, or $BaCO_3$?
b. To remove CO_2 from the atmosphere in a space capsule, would you use MgO, CaO, or BaO?
c. As a component of the alloy in an automotive spark plug electrode, would you use Be, Ca, or Ba?

Given: application and selected alkaline earth metals

Asked for: most appropriate substance for each application

Strategy:

Based on the discussion in this section and any relevant information elsewhere in this book, determine which substance is most appropriate for the indicated use.

Solution

a. All the alkaline earth carbonates will neutralize an acidic solution by Equation 21.3.7. Because beryllium and its salts are toxic, however, $BeCO_3$ cannot be used as an antacid. Of the remaining choices, $CaCO_3$ is somewhat more soluble than $BaCO_3$ (according to the K_{sp} values in Table 17.1), suggesting that it will act more rapidly. Moreover, the formula mass of $CaCO_3$ is 100.1 amu, whereas that of $BaCO_3$ is almost twice as large. Therefore, neutralizing a given amount of acid would require twice the mass of $BaCO_3$ compared with $CaCO_3$. Furthermore, reaction of $BaCO_3$ with acid produces a solution containing Ba^{2+} ions, which are toxic. (Ba^{2+} is a stimulant that can cause ventricular fibrillation of the heart.) Finally, $CaCO_3$ is produced on a vast scale, so $CaCO_3$ is likely to be significantly less expensive than any barium compound. Consequently, $CaCO_3$ is the best choice for an antacid.
b. This application involves reacting CO_2 with an alkaline earth oxide to form the carbonate, which is the reverse of the thermal decomposition reaction in which MCO_3 decomposes to CO_2 and the metal oxide MO (Equation 21.3.5). Owing to their higher lattice energies, the smallest alkaline earth metals should form the most stable oxides. Hence their carbonates should decompose at the lowest temperatures, as is observed ($BeCO_3$ decomposes at 100°C; $BaCO_3$ at 1360°C). If the carbonate with the smallest alkaline earth metal decomposes most readily, we would expect the reverse reaction (formation of a carbonate) to occur most readily with the largest metal cation (Ba^{2+}). Hence BaO is the best choice.
c. The alloy in a spark plug electrode must release electrons and promote their flow across the gap between the electrodes at high temperatures. Of the three metals listed, Ba has the lowest ionization energy and thus releases electrons most readily. Heating a barium-containing alloy to high temperatures will cause some ionization to occur, providing the initial step in forming a spark.

Exercise 21.3.1

Which of the indicated alkaline earth metals or their compounds is most appropriate for each application?

a. drying agent for removing water from the atmosphere—$CaCl_2$, $MgSO_4$, or BaF_2
b. removal of scale deposits (largely $CaCO_3$) in water pipes—HCl(aq) or H_2SO_4(aq)
c. removal of traces of N_2 from purified argon gas—Be, Ca, or Ba

Answer

a. $MgSO_4$
b. HCl
c. Ba

Example 21.3.2

Predict the products of each reaction and then balance each chemical equation.

a. CaO(s) + HCl(g) →
b. MgO(s) + excess OH^-(aq) →
c. $\mathrm{CaH_2(s) + TiO_2(s) \xrightarrow{\Delta}}$

Given: reactants

Asked for: products and balanced chemical equation

Strategy:

Follow the procedure given in Example 3 to predict the products of each reaction and then balance each chemical equation.

Solution

a. **A** Gaseous HCl is an acid, and CaO is a basic oxide that contains the O^{2-} ion. This is therefore an acid–base reaction that produces $CaCl_2$ and H_2O.

B The balanced chemical equation is

$$CaO_{(s)} + 2HCl_{(g)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)} \tag{21.3.12}$$

b. **A** Magnesium oxide is a basic oxide, so it can either react with water to give a basic solution or dissolve in an acidic solution. Hydroxide ion is also a base. Because we have two bases but no acid, an acid–base reaction is impossible. A redox reaction is not likely because MgO is neither a good oxidant nor a good reductant.

B We conclude that no reaction occurs.

c. **A** Because CaH_2 contains the hydride ion (H^-), it is a good reductant. It is also a strong base because H^- ions can react with H^+ ions to form H_2. Titanium oxide (TiO_2) is a metal oxide that contains the metal in its highest oxidation state (+4 for a group 4 metal); it can act as an oxidant by accepting electrons. We therefore predict that a redox reaction will occur, in which H^- is oxidized and Ti^{4+} is reduced. The most probable reduction product is metallic titanium, but what is the oxidation product? Oxygen must appear in the products, and both CaO and H_2O are stable compounds. The +1 oxidation state of hydrogen in H_2O is a sign that an oxidation has occurred ($2H^- \rightarrow 2H^+ + 4e^-$).

B The balanced chemical equation is

$$\mathrm{CaH_2(s) + TiO_2(s) \xrightarrow{\Delta} Ti(s) + CaO(s) + H_2O(l)}$$

We could also write the products as Ti(s) + $Ca(OH)_2$(s).

Exercise 21.3.2

Predict the products of each reaction and then balance each chemical equation.

a. $\mathrm{BeCl_2(s) + Mg(s) \xrightarrow{\Delta}}$
b. $BaCl_2$(aq) + Na_2SO_4(aq) →
c. BeO(s) + OH^-(aq) + H_2O(l) →

Answer

a. $\mathrm{BeCl_2(s) + Mg(s) \xrightarrow{\Delta} Be(s) + MgCl_2(s)}$
b. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$
c. $BeO(s) + 2OH^-(aq) + H_2O(l) \rightarrow [Be(OH)_4]^{2-}(aq)$

Summary

Group 2 elements almost exclusively form ionic compounds containing the M^{2+} ion, they are more reactive toward group 15 elements, and they have a greater tendency to form complexes with Lewis bases than do the alkali metals. Pure samples of most of the alkaline earth metals can be obtained by electrolysis of the chlorides or oxides. Beryllium was first obtained by the reduction of its chloride; radium chloride, which is radioactive, was obtained through a series of reactions and separations. In contrast to the alkali metals, the alkaline earth metals generally have little or no affinity for an added electron. All alkaline earth metals react with the halogens to produce the corresponding halides, with oxygen to form the oxide (except for barium, which forms the peroxide), and with the heavier chalcogens to form chalcogenides or polychalcogenide ions. All oxides except BeO react with CO_2 to form carbonates, which in turn react with acid to produce CO_2 and H_2O. Except for Be, all the alkaline earth metals react with N_2 to form nitrides, and all react with carbon and hydrogen to form carbides and hydrides. Alkaline earth metals dissolve in liquid ammonia to give solutions that contain two solvated electrons per metal atom. The alkaline earth metals have a greater tendency than the alkali metals to form complexes with crown ethers, cryptands, and other Lewis bases. The most important alkaline earth organometallic compounds are Grignard reagents (RMgX), which are used to synthesize organic compounds.

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21.4: Group 13: The Boron Family

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.

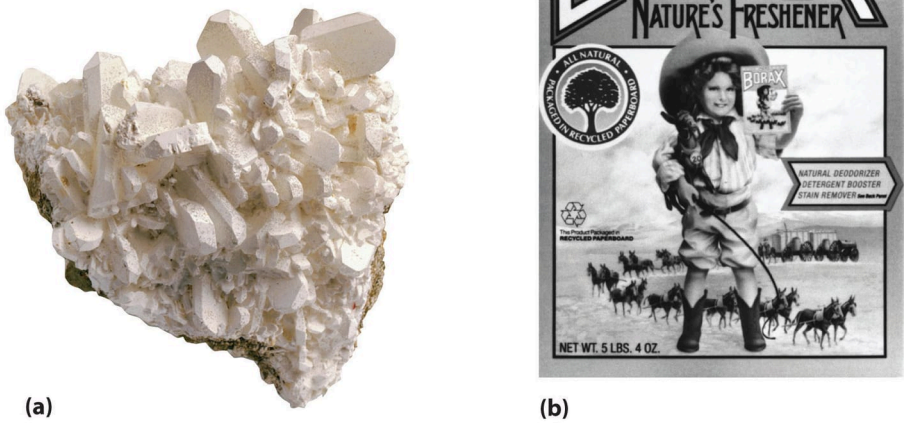


Figure 21.4.1: Borax Deposits. *(a) Concentrated deposits of crystalline borax [$Na_2B_4O_5(OH)_4{\cdot}8H_2O$] are found in ancient lake beds, such as the Mojave Desert and Death Valley in the western United States. (b) Borax is used in various cleaning products, including 20 Mule Team Borax, a laundry 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 21.4.1) 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:

$$\mathrm{Na_2B_4O_5(OH)_4 \cdot 8H_2O(s) \xrightarrow{acid} B(OH)_3(s) \xrightarrow{\Delta} B_2O_3(s)} \tag{21.4.1}$$

$$\mathrm{B_2O_3(s) + 3Mg(s) \xrightarrow{\Delta} 2B(s) + 3MgO(s)} \tag{21.4.2}$$

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):

$$\mathrm{BCl_3(g) + \frac{3}{2}H_2(g) \rightarrow B(s) + 3HCl(g)} \tag{21.4.3}$$

$$B_2H_{6(g)} \rightarrow 2B_{(s)} + 3H_{2(g)} \tag{21.4.4}$$

The reaction shown in Equation 21.4.3 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 $Al(OH)_3$:

$$2[Al(OH)_4]^-_{(aq)} + CO_{2(g)} \rightarrow 2Al(OH)_{3(s)} + CO^{2-}_{3(aq)} + H_2O_{(l)} \tag{21.4.5}$$

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.

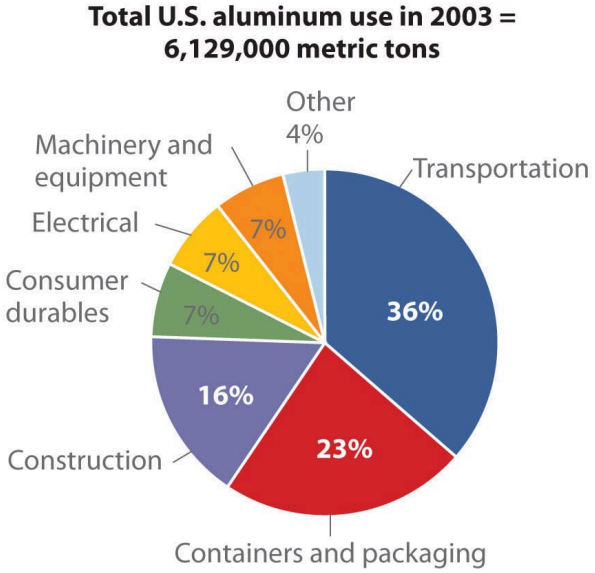


Figure 21.4.2: Source: Thomas D. Kelly and Grecia R. Matos, “Historical Statistics for Mineral and Material Commodities in the United States,” US Geological Survey Data Series 140, 2010, accessed July 20, 2011, pubs.usgs.gov/ds/2005/140/.

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 21.4.1 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 21.4.1: 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.

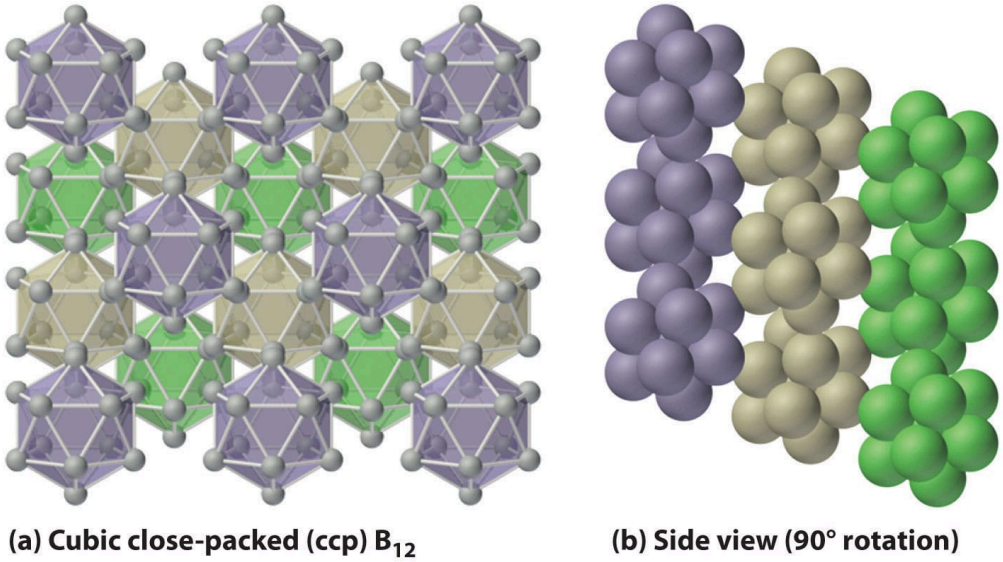


Figure 21.4.3: Solid Boron Contains B_{12} Icosahedra. Unlike metallic solids, elemental boron consists of a regular array of B_{12} icosahedra rather than individual boron atoms. Note that each boron atom in the B_{12} icosahedron is connected to five other boron atoms within the B_{12} unit. (a) The 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 21.4.3). 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 21.4.6); boron oxide (B_2O_3), which is formed when boron is heated with excess oxygen (Equation 21.4.7); and the boron trihalides (BX_3), which are formed by heating boron with excess halogen (Equation 21.4.8).

$$2B(s) + N_2(g) \xrightarrow{\Delta} 2BN(s) \tag{21.4.6}$$

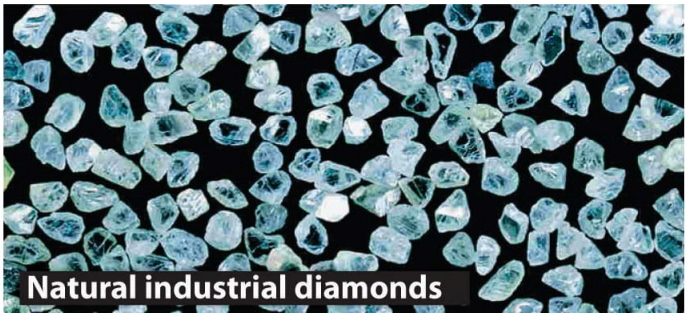
$$4B(s) + 3O_2(g) \xrightarrow{\Delta} 2B_2O_3(s) \tag{21.4.7}$$

$$2B(s) + 3X_2(g) \xrightarrow{\Delta} 2BX_3(g) \tag{21.4.8}$$

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 21.4.4. 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.

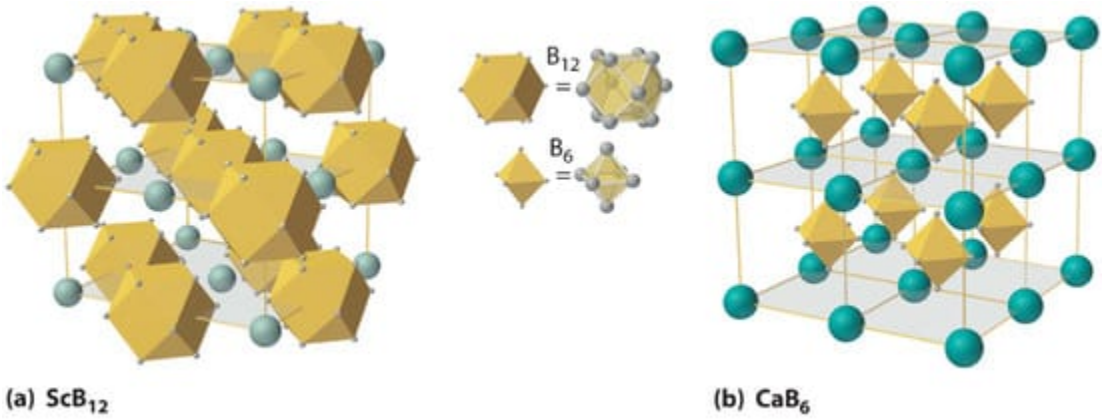


Figure 21.4.4: The Structures of $ScB_{12}$and CaB_6, Two Boron-Rich Metal Borides. *(a) The structure of ScB_{12} consists of B_{12} clusters and Sc atoms arranged in a faced-centered cubic lattice similar to that of NaCl, with B_{12}units occupying the anion positions and scandium atoms the cation 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 21.4.5. 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.

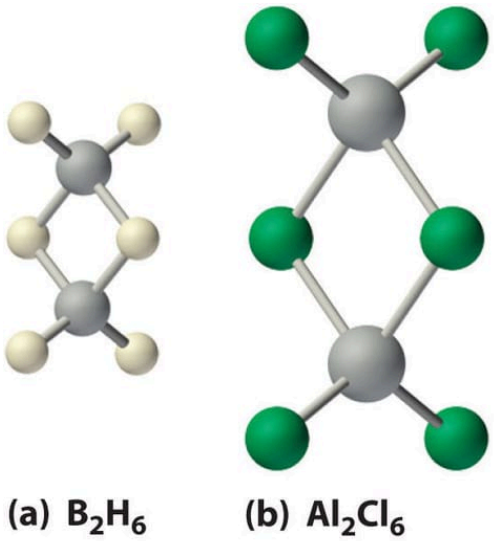
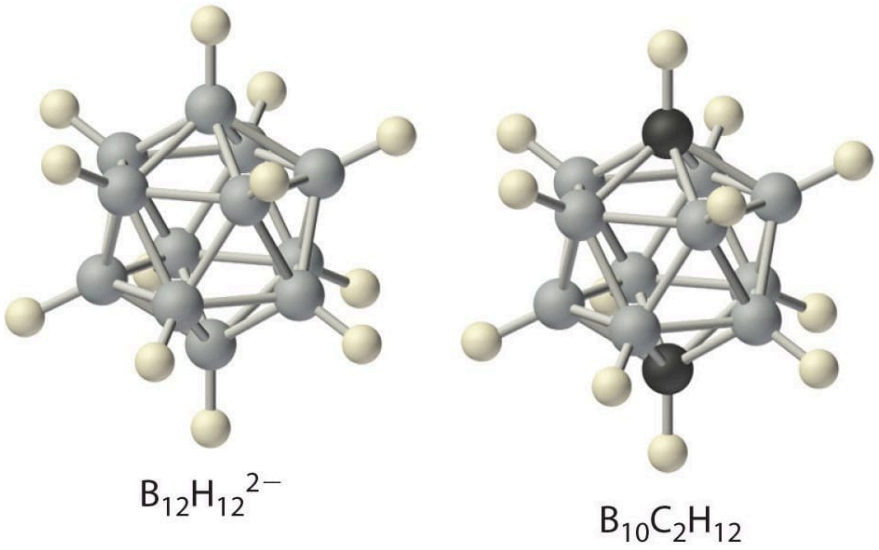


Figure 21.4.5: The Structures of Diborane (B_2H_6) and Aluminum Chloride (Al_2Cl_6). (a) The hydrogen-bridged dimer B_2H_6 contains two three-center, two-electron bonds as described for the $B_2H_7^-$ ion in Figure 21.5. (b) In contrast, the bonding in the halogen-bridged dimer Al_2Cl_6 can be described 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:

$$B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(s)} + 3H_2O(l) \qquad \Delta H_{comb} = -2165\ kJ/mol \tag{21.4.9}$$

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 21.4.1

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 21.4.1

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:

$$2M_{(s)} + 3X_{2(s,l,g)} \rightarrow 2MX_{3(s)} \text{ or } M_2X_6 \tag{21.4.10}$$

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 21.4.4). 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:

$$Al_2Cl_{6(soln)} + 2(CH_3)_3N_{(soln)} \rightarrow 2(CH_3)_3N : AlCl_{3(soln)} \tag{21.4.11}$$

In water, the halides of the group 13 metals hydrolyze to produce the metal hydroxide (\[M(OH)_3\]):

$$MX_{3(s)} + 3H_2O_{(l)} \rightarrow M(OH)_{3(s)} + 3HX_{(aq)} \tag{21.4.12}$$

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 21.4.7), 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:

$$4\mathrm{M(s)} + 3\mathrm{O_2(g)} \xrightarrow{\Delta} 2\mathrm{M_2O_3(s)} \tag{21.4.13}$$

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.

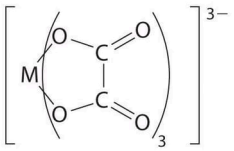
All group 13 oxides dissolve in dilute acid, but Al_2O_3 and Ga_2O_3 are amphoteric.

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.

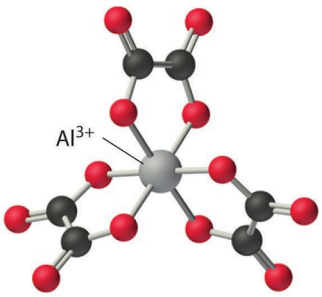
Complexes of Group 13 Elements

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:

$$[M(H_2O)_6]^{3+}_{(aq)} \rightarrow M(H_2O)_5(OH)^{2+}_{(aq)} + H^+_{(aq)} \tag{21.4.14}$$



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 21.4.2

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 21.4.2

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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21.5: Group 14: The Carbon Family

Learning Objectives

- To understand the trends in properties and reactivity of the group 14 elements.

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 21.5.1). 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.



(a) (b)

Figure 21.5.1: 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.*

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.

Preparation and General Properties of the Group 14 Elements

The natural abundance of the group 14 elements varies tremendously. 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:

$$\mathrm{SiO_2(s) + 3C(s) \xrightarrow{\Delta} SiC(s) + 2CO(g)} \tag{21.5.1}$$

$$\mathrm{SiC(s) \xrightarrow{\Delta} Si(s) + C(graphite)} \tag{21.5.2}$$

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 (part (a) in Figure 21.5.2). 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 21.5.2: 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. (b) 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.

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:

$$\mathrm{SiCl_4(l) + 2H_2(g) \xrightarrow{\Delta} Si(s) + 4HCl(g)} \tag{21.5.3}$$

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 (part (b) in Figure 21.5.2).

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:

$$\mathrm{PbS(s)} + \frac{3}{2}\mathrm{O_2(g)} \xrightarrow{\Delta} \mathrm{PbO(s)} + \mathrm{SO_2(g)} \tag{21.5.4}$$

$$\mathrm{PbO(s)} + \mathrm{C(s)} \xrightarrow{\Delta} \mathrm{Pb(l)} + \mathrm{CO(g)} \tag{21.5.5}$$

or

$$\mathrm{PbO(s)} + \mathrm{CO(g)} \xrightarrow{\Delta} \mathrm{Pb(l)} + \mathrm{CO_2(g)} \tag{21.5.6}$$

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 21.5.1 "Selected Properties of the Group 14 Elements" 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 21.5.1: Selected Properties of the Group 14 Elements

Property	Carbon	Silicon	Germanium	Tin	Lead
atomic symbol	C	Si	Ge	Sn	Pb
***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.					

Property	Carbon	Silicon	Germanium	Tin	Lead
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 Carbon

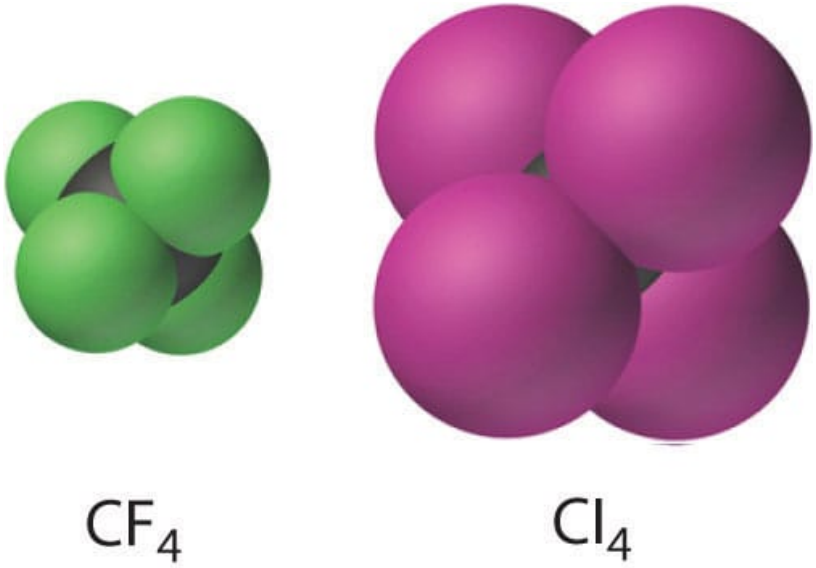
Carbon is the building block of all organic compounds, including biomolecules, fuels, pharmaceuticals, and plastics, whereas inorganic compounds of carbon include metal carbonates, which are found in substances as diverse as fertilizers and antacid tablets, halides, oxides, carbides, and carboranes. 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 (Figure 7.18). 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:

$$CH_{4(g)} + 4X_{2(g)} \rightarrow CX_{4(l,s)} + 4HX_{(g)} \tag{21.5.7}$$



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:

$$\mathrm{HCO_2H(l)} \xrightarrow{\mathrm{H_2SO_4(l)}} \mathrm{CO(g) + H_3O^+(aq) + HSO_4^-} \tag{21.5.8}$$

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:

$$\mathrm{CO(g) + Cl_2(g)} \xrightarrow{\Delta} \mathrm{Cl_2C{=}O(g)} \tag{21.5.9}$$

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):

$$\mathrm{C(s) + 2S(g) \xrightarrow{\Delta} CS_2(g)} \tag{21.5.10}$$

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^{4-} 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 ???) 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 21.5.1

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 21.5.1

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. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow CO_2(g) + NaHSO_4(aq) + H_2O(l)$

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 21.5.1*: 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):

$$MX_{4(s,l)} + 2H_2O_{(l)} \rightarrow MO_{2(s)} + 4HX_{(aq)} \tag{21.5.11}$$

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 21.5.3). 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.

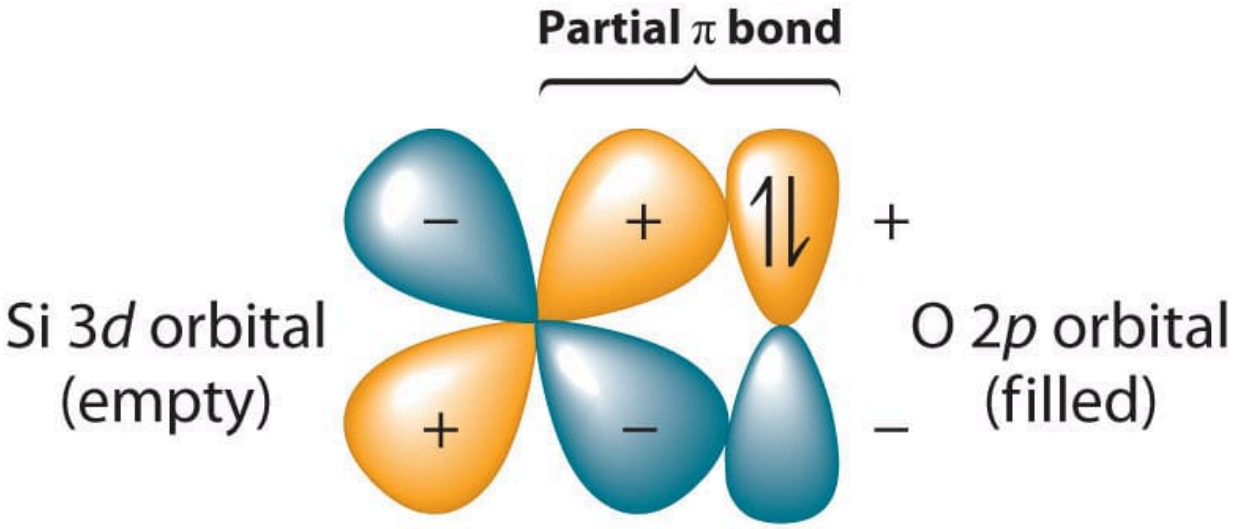
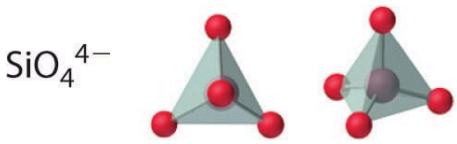


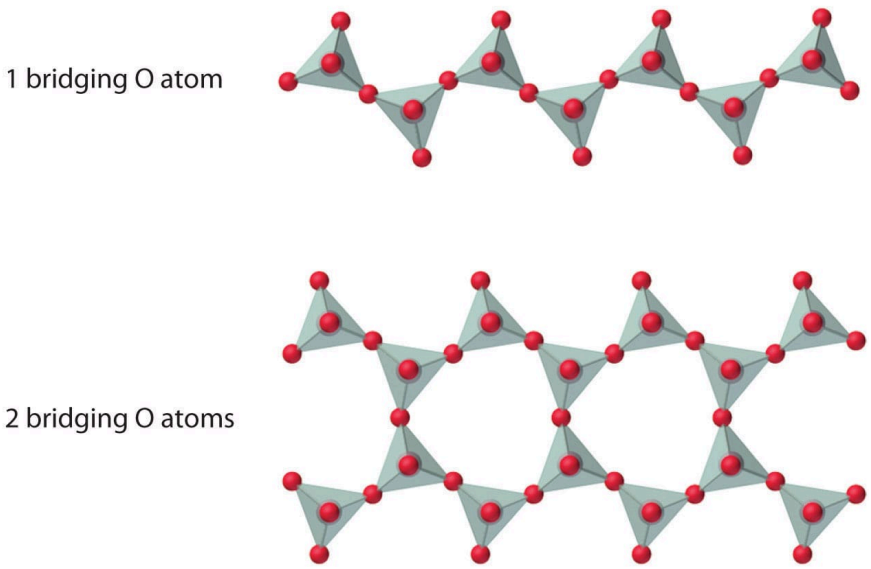
Figure 21.5.3: π Bonding between Silicon and Oxygen. Silicon has relatively low-energy, empty 3d orbitals that can interact with filled 2p hybrid orbitals on oxygen. This interaction results in a partial π bond in which both electrons are supplied by oxygen, giving the Si–O bond partial double bond character 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.



In a large and important class of materials called aluminosilicates, some of the Si atoms are replaced by Al atoms to give aluminosilicates such as zeolites, whose three-dimensional framework structures have large cavities connected by smaller tunnels (Figure 21.5.4). 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.

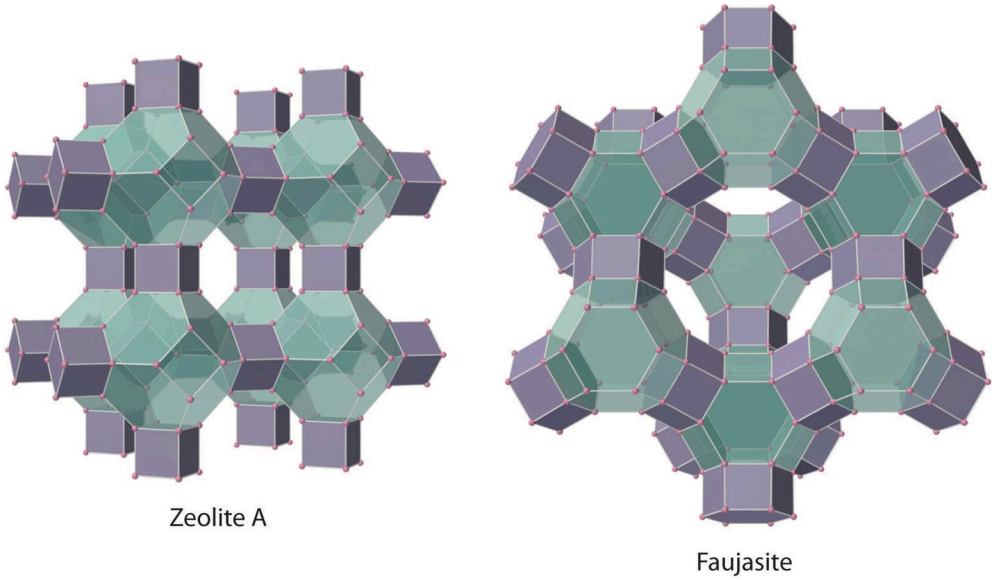


Figure 21.5.4: Zeolites Are Aluminosilicates with Large Cavities Connected by Channels. The cavities normally contain hydrated cations that are loosely bound to the oxygen atoms of the negatively charged framework by electrostatic interactions. The sizes and arrangements of the channels and cavities 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):

$$3Si_{(l)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} \tag{21.5.12}$$

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:

$$Mg_2Si_{(s)} + 4H^+_{(aq)} \rightarrow 2Mg^{2+}_{(aq)} + SiH_{4(g)} \tag{21.5.13}$$

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. (Example 6 in Section 22.3 examines this 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.

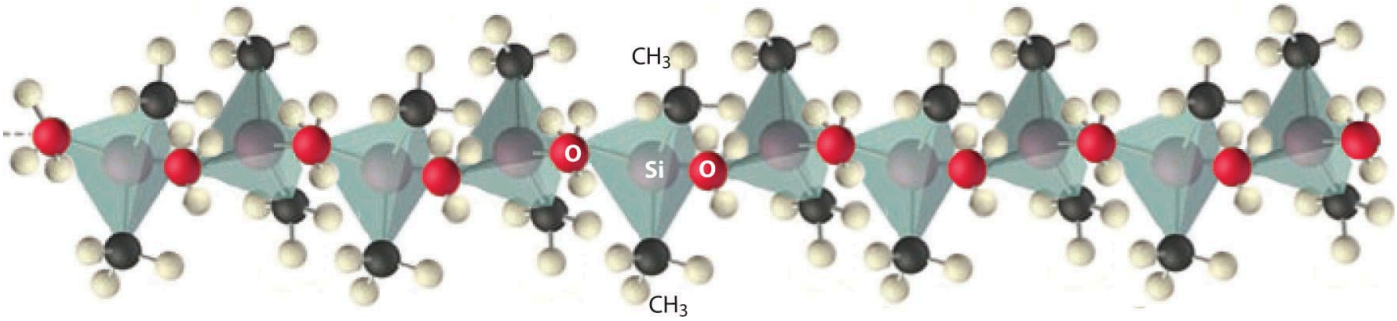


Figure 21.5.5 Silicones Are Polymers with Long Chains of Alternating Silicon and Oxygen Atoms. The structure of a linear silicone polymer is similar to that of quartz, but two of the oxygen atoms attached to each silicon atom are replaced by the carbon atoms of organic groups, such as the methyl groups (–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 21.5.5). 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 21.5.2

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 21.5.2

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. $PbO_2(s) \xrightarrow{\Delta} PbO(s) + \frac{1}{2}O_2(g)$
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. The group 14 elements show the greatest range of chemical behavior of any group in the periodic table. 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. 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. 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.

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21.E: Exercises

21.1: Periodic Trends and Charge Density

Problems

1. List three physical properties that are important in describing the behavior of the main group elements.
2. Arrange K, Cs, Sr, Ca, Ba, and Li in order of

    a. increasing ionization energy.
    b. increasing atomic size.
    c. increasing electronegativity.

3. Arrange Rb, H, Be, Na, Cs, and Ca in order of

    a. decreasing atomic size.
    b. decreasing magnitude of electron affinity.

4. Which periodic trends are affected by Z_{eff}? Based on the positions of the elements in the periodic table, which element would you expect to have the highest Z_{eff}? the lowest Z_{eff}?

5. Compare the properties of the metals and nonmetals with regard to their electronegativities and preferred oxidation states.

6. Of Ca, Br, Li, N, Zr, Ar, Sr, and S, which elements have a greater tendency to form positive ions than negative ions?

7. Arrange As, O, Ca, Sn, Be, and Sb in order of decreasing metallic character.

8. Give three reasons the chemistry of the second-period elements is generally not representative of their groups as a whole.

9. Compare the second-period elements and their heavier congeners with regard to
    a. magnitude of electron affinity.
    b. coordination number.
    c. the solubility of the halides in nonpolar solvents.

10. The heavier main group elements tend to form extended sigma-bonded structures rather than multiple bonds to other atoms. Give a reasonable explanation for this tendency.

11. What is the diagonal effect? How does it explain the similarity in chemistry between, for example, boron and silicon?

12. Although many of the properties of the second- and third-period elements in a group are quite different, one property is similar. Which one?

13. Two elements are effective additives to solid rocket propellant: beryllium and one other element that has similar chemistry. Based on the position of beryllium in the periodic table, identify the second element.

14. Give two reasons for the inert-pair effect. How would this phenomenon explain why Sn^{2+} is a better reducing agent than Pb^{2+}?

15. Explain the following trend in electron affinities: Al (−41.8 kJ/mol), Si (−134.1 kJ/mol), P (−72.0 kJ/mol), and S (−200.4 kJ/mol).

16. Using orbital energy arguments, explain why electron configurations with more than four electron pairs around the central atom are not observed for second-period elements.

Answers

3.

a. Cs > Rb > Ca > Na > Be > H
b. H > Na > Rb > Cs > Ca > Be

7. Ca > Be > Sn > Sb > As > O

13. aluminum

15. The magnitude of electron affinity increases from left to right in a period due to the increase in Z_{eff}; P has a lower electron affinity than expected due to its half-filled 3p shell, which requires the added electron to enter an already occupied 3p orbital.

Structure and Reactivity

1. The following table lists the valences, coordination numbers, and ionic radii for a series of cations. Which would you substitute for K^+ in a crystalline lattice? Explain your answer.

Metal	Charge	Coordination Number	Ionic Radius (pm)
Li	+1	4	76
Na	+1	6	102
K	+1	6	138
Mg	+2	6	72
Ca	+2	6	100
Sr	+2	6	118

Answer

1. Sr^{2+}; it is the ion with the radius closest to that of K^+.

21.2: Group 1: The Alkali Metals

Problems

1. Which of the group 1 elements reacts least readily with oxygen? Which is most likely to form a hydrated, crystalline salt? Explain your answers.
2. The alkali metals have a significant electron affinity, corresponding to the addition of an electron to give the M^- anion. Why, then, do they commonly lose the ns^1electron to form the M^+ cation rather than gaining an electron to form M^-?
3. Lithium is a far stronger reductant than sodium; cesium is almost as strong as lithium, which does not agree with the expected periodic trend. What two opposing properties explain this apparent anomaly? Is the same anomaly found among the alkaline earth metals?
4. Explain why the ionic character of LiCl is less than that of NaCl. Based on periodic trends, would you expect the ionic character of $BeCl_2$ to be greater or less than that of LiCl? Why?
5. Alkali metals and carbon form intercalation compounds with extremely high electrical conductivity. Is this conductivity through the layers or along the layers? Explain your answer.
6. Electrolysis is often used to isolate the lighter alkali metals from their molten halides. Why are halides used rather than the oxides or carbonates, which are easier to isolate? With this in mind, what is the purpose of adding calcium chloride to the alkali metal halide?
7. The only alkali metal that reacts with oxygen to give a compound with the expected stoichiometry is lithium, which gives Li_2O. In contrast, sodium reacts with oxygen to give Na_2O_2, and the heavier alkali metals form superoxides. Explain the difference in the stoichiometries of these products.

8. Classify aqueous solutions of Li_2O, Na_2O, and CsO_2 as acidic, basic, or amphoteric.
9. Although methanol is relatively unreactive, it can be converted to a synthetically more useful form by reaction with LiH. Predict the products of reacting methanol with LiH. Describe the visual changes you would expect to see during this reaction.
10. Lithium reacts with atmospheric nitrogen to form lithium nitride (Li_3N). Why do the other alkali metals not form analogous nitrides? Explain why all the alkali metals react with arsenic to form the corresponding arsenides (M_3As).

Structure and Reactivity

1. Write a balanced chemical equation to describe each reaction.

    a. the electrolysis of fused (melted) sodium chloride
    b. the thermal decomposition of $KClO_3$
    c. the preparation of hydrogen fluoride from calcium fluoride and sulfuric acid
    d. the oxidation of sodium metal by oxygen

2. What products are formed at the anode and the cathode during electrolysis of

    a. molten lithium hydride?
    b. molten lithium chloride?
    c. aqueous sodium fluoride?

Write the corresponding half-reactions for each reaction.

3. Sodium metal is prepared by electrolysis of molten NaCl. If 25.0 g of chlorine gas are produced in the electrolysis of the molten salt using 9.6 A (C/s) of current, how many hours were required for the reaction? What mass of sodium was produced?

4. Sodium peroxide can remove CO_2 from the air and replace it with oxygen according to the following unbalanced chemical equation:

$$Na_2O_2(s) + CO_2(g) \rightarrow Na_2CO_3(s) + O_2(g)$$

    a. Balance the chemical equation.
    b. Identify each oxidation and reduction half-reaction.
    c. Assuming complete reaction, what will be the pressure inside a sealed 1.50 L container after reacting excess sodium peroxide with carbon dioxide that was initially at 0.133 atm and 37°C?

5. Predict the products of each chemical reaction and then balance each chemical equation.

    a. $K(s) + CH_3CH_2OH(l) \rightarrow$
    b. $Na(s) + CH_3CO_2H(l) \rightarrow$
    c. $NH_4Cl(s) + Li(s) \rightarrow$
    d. $(CH_3)_2NH(l) + K(s) \rightarrow$

6. Predict the products of each reaction.

    a. an alkyl chloride with lithium metal
    b. rubidium with oxygen

7. A 655 mg sample of graphite was allowed to react with potassium metal, and 744 mg of product was isolated. What is the stoichiometry of the product?

8. Perchloric acid, which is used as a reagent in a number of chemical reactions, is typically neutralized before disposal. When a novice chemist accidentally used K_2CO_3 to neutralize perchloric acid, a large mass of $KClO_4$ ($K_{sp} = 1.05 \times 10^{-2}$) precipitated from solution. What mass of potassium ion is present in 1.00 L of a saturated solution of $KClO_4$?

9. A key step in the isolation of the alkali metals from their ores is selective precipitation. For example, lithium is separated from sodium and potassium by precipitation of Li_2CO_3 ($K_{sp} = 8.15 \times 10^{-4}$). If 500.0 mL of a 0.275 M solution of Na_2CO_3 are added to 500.0 mL of a 0.536 M lithium hydroxide solution, what mass of Li_2CO_3 will precipitate (assuming no further

reactions occur)? What mass of lithium will remain in solution?

Answer

9. 5.54 g Li_2CO_3; 0.82 g Li^+

21.3: Group 2: The Alkaline Earth Metals

Problems

1. The electronegativities of Li and Sr are nearly identical (0.98 versus 0.95, respectively). Given their positions in the periodic table, how do you account for this?
2. Arrange Na, Ba, Cs, and Li in order of increasing Z_{eff}.
3. Do you expect the melting point of NaCl to be greater than, equal to, or less than that of $MgCl_2$? Why?
4. Which of the group 2 elements would you expect to form primarily ionic rather than covalent organometallic compounds? Explain your reasoning.
5. Explain why beryllium forms compounds that are best regarded as covalent in nature, whereas the other elements in group 2 generally form ionic compounds.
6. Why is the trend in the reactions of the alkaline earth metals with nitrogen the reverse of the trend seen for the alkali metals?
7. Is the bonding in the alkaline earth hydrides primarily ionic or covalent in nature? Explain your answer. Given the type of bonding, do you expect the lighter or heavier alkaline earth metals to be better reducing agents?
8. Using arguments based on ionic size, charge, and chemical reactivity, explain why beryllium oxide is amphoteric. What element do you expect to be most similar to beryllium in its reactivity? Why?
9. Explain why the solubility of the carbonates and sulfates of the alkaline earth metals decreases with increasing cation size.
10. Beryllium oxide is amphoteric, magnesium oxide is weakly basic, and calcium oxide is very basic. Explain how this trend is related to the ionic character of the oxides.
11. Do you expect the ΔH_f° of CaH_2 to be greater than, the same as, or less than that of BaH_2? Why or why not?
12. Which of the s-block elements would you select to carry out a chemical reduction on a small scale? Consider cost, reactivity, and stability in making your choice. How would your choice differ if the reduction were carried out on an industrial scale?

Structure and Reactivity

1. Beryllium iodide reacts vigorously with water to produce HI. Write a balanced chemical equation for this reaction and explain why it is violent.
2. Predict the products of each reaction and then balance each chemical equation.

    a. $Mg(OH)_2(aq) + (NH_4)_3PO_4(aq) \rightarrow$
    b. calcium carbonate and sulfuric acid →
    c. $CaCl_2(aq) + Na_3PO_4(aq) \rightarrow$
    d. the thermal decomposition of $SrCO_3$

3. Predict the products of each reaction and then balance each chemical equation.
    a. $Sr(s) + O_2(g) \rightarrow$
    b. the thermal decomposition of $CaCO_3(s)$
    c. $CaC_2(s) + H_2O(l) \rightarrow$
    d. $RbHCO_3(s) + H_2SO_4(aq) \rightarrow$

4. Indicate whether each pair of substances will react and, if so, write a balanced chemical equation for the reaction.
    a. an alkyl chloride and magnesium metal
    b. strontium metal and nitrogen
    c. magnesium metal and cold water
    d. beryllium and nitrogen

5. Using a thermodynamic cycle and information presented in Chapter 7 and Chapter 8, calculate the lattice energy of magnesium nitride (Mg_3N_2). (ΔH_f° for Mg_3N_2 is –463 kJ/mol, and ΔH° for $N(g) + 3e^- \rightarrow N^{3-}$ is +1736 kJ.) How does the

lattice energy of Mg_3N_2 compare with that of $MgCl_2$ and MgO? (See Chapter 25 for the enthalpy of formation values.)

6. The solubility products of the carbonate salts of magnesium, calcium, and strontium are 6.82×10^{-6}, 3.36×10^{-9}, and 5.60×10^{-10}, respectively. How many milligrams of each compound would be present in 200.0 mL of a saturated solution of each? How would the solubility depend on the pH of the solution? Why?

7. The solubility products of $BaSO_4$ and $CaSO_4$ are 1.08×10^{-10} and 4.93×10^{-5}, respectively. What accounts for this difference? When 500.0 mL of a solution that contains 1.00 M $Ba(NO_3)_2$ and 3.00 M $Ca(NO_3)_2$ is mixed with a 2.00 M solution of Na_2SO_4, a precipitate forms. What is the identity of the precipitate? How much of it will form before the second salt precipitates?

8. Electrolytic reduction is used to produce magnesium metal from $MgCl_2$. The goal is to produce 200.0 kg of Mg by this method.
   a. How many kilograms of $MgCl_2$ are required?
   b. How many liters of chlorine gas will be released at standard temperature and pressure?
   c. How many hours will it take to process the magnesium metal if a total current of 1.00×10^4 A is used?

9. A sample consisting of 20.35 g of finely divided calcium metal is allowed to react completely with nitrogen. What is the mass of the product?

10. What mass of magnesium hydride will react with water to produce 1.51 L of hydrogen gas at standard temperature and pressure?

Answers

3

   a. $2Sr(s) + O_2(g) \rightarrow 2SrO(s)$
   b. $\mathrm{CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)}$
   c. $CaC_2(s) + 2H_2O(l) \rightarrow C_2H_2(g) + Ca(OH)_2(aq)$
   d. $2RbHCO_3(s) + H_2SO_4(aq) \rightarrow Rb_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$

7. The Ba^{2+} ion is larger and has a lower hydration energy than the Ca^{2+} ion. The precipitate is $BaSO_4$; 117 g of $BaSO_4$.

9. 25.09 g of Ca_3N_2

21.4: Group 13: The Boron Family

Conceptual Problems

1. None of the group 13 elements was isolated until the early 19th century, even though one of these elements is the most abundant metal on Earth. Explain why the discovery of these elements came so late and describe how they were finally isolated.
2. Boron and aluminum exhibit very different chemistry. Which element forms complexes with the most ionic character? Which element is a metal? a semimetal? What single property best explains the difference in their reactivity?
3. The usual oxidation state of boron and aluminum is +3, whereas the heavier elements in group 13 have an increasing tendency to form compounds in the +1 oxidation state. Given that all group 13 elements have an ns^2np^1 electron configuration, how do you explain this difference between the lighter and heavier group 13 elements?
4. Do you expect the group 13 elements to be highly reactive in air? Why or why not?
5. Which of the group 13 elements has the least metallic character? Explain why.
6. Boron forms multicenter bonds rather than metallic lattices with delocalized valence electrons. Why does it prefer this type of bonding? Does this explain why boron behaves like a semiconductor rather than a metal? Explain your answer.
7. Because the B–N unit is isoelectronic with the C–C unit, compounds that contain these units tend to have similar chemistry, although they exhibit some important differences. Describe the differences in physical properties, conductivity, and reactivity

of these two types of compounds.

8. Boron has a strong tendency to form clusters. Does aluminum have this same tendency? Why or why not?
9. Explain why a B–O bond is much stronger than a B–C bond.
10. The electron affinities of boron and aluminum are −27 and −42 kJ/mol, respectively. Contrary to the usual periodic trends, the electron affinities of the remaining elements in group 13 are between those of B and Al. How do you explain this apparent anomaly?
11. The reduction potentials of B and Al in the +3 oxidation state are −0.87 V and −1.66 V, respectively. Do you expect the reduction potentials of the remaining elements of group 13 to be greater than or less than these values? How do you explain the differences between the expected values and those given in Table $21.E.1$ "Selected Properties of the Group 13 Elements"?
12. The compound Al_2Br_6 is a halide-bridged dimer in the vapor phase, similar to diborane (B_2H_6). Draw the structure of Al_2Br_6 and then compare the bonding in this compound with that found in diborane. Explain the differences.
13. The compound AlH_3 is an insoluble, polymeric solid that reacts with strong Lewis bases, such as Me_3N, to form adducts with 10 valence electrons around aluminum. What hybrid orbital set is formed to allow this to occur?

Answers

1. The high stability of compounds of the group 13 elements with oxygen required powerful reductants such as metallic potassium to be isolated. Al and B were initially prepared by reducing molten $AlCl_3$ and B_2O_3, respectively, with potassium.

5. Due to its low electronegativity and small size, boron is an unreactive semimetal rather than a metal.

7. The B–N bond is significantly more polar than the C–C bond, which makes B–N compounds more reactive and generally less stable than the corresponding carbon compounds. Increased polarity results in less delocalization and makes the planar form of BN less conductive than graphite.

9. Partial pi bonding between O and B increases the B–O bond strength.

11. Periodic trends predict that the cations of the heavier elements should be easier to reduce, so the elements should have less negative reduction potentials. In fact, the reverse is observed because the heavier elements have anomalously high Z_{eff} values due to poor shielding by filled (n – 1)d and (n – 2)f subshells.

13. dsp^3

Structure and Reactivity

1. Is $B(OH)_3$ a strong or a weak acid? Using bonding arguments, explain why.
2. Using bonding arguments, explain why organoaluminum compounds are expected to be potent Lewis acids that react rapidly with weak Lewis bases.
3. Imagine that you are studying chemistry prior to the discovery of gallium, element 31. Considering its position in the periodic table, predict the following properties of gallium:

    a. chemical formulas of its most common oxide, most common chloride, and most common hydride
    b. solubility of its oxide in water and the acidity or basicity of the resulting solution
    c. the principal ion formed in aqueous solution

4. The halides of Al, Ga, In, and Tl dissolve in water to form acidic solutions containing the hydrated metal ions, but only the halides of aluminum and gallium dissolve in aqueous base to form soluble metal-hydroxide complexes. Show the formulas of the soluble metal–hydroxide complexes and of the hydrated metal ions. Explain the difference in their reactivities.
5. Complete and balance each chemical equation.

    a. $BCl_3(g) + H_2(g) \xrightarrow{\Delta}$
    b. $6C_2H_4(g) + B_2H_6(g) \rightarrow$
    c. $B_2H_6(g) + 3Cl_2(g) \rightarrow$
    d. $B_2H_6(g) + 2(C_2H_5)_2S(g) \rightarrow$

6. Complete and balance each chemical equation.
    a. $BBr_3(g) + H_2(g) \xrightarrow{\Delta}$

b. $BF_3(g) + F^-(g) \rightarrow$
c. $LiH(s) + B_2H_6(g) \rightarrow$
d. $B(OH)_3(s) + NaOH(aq) \rightarrow$

7. Write a balanced chemical equation for each reaction.
   a. the dissolution of Al_2O_3 in dilute acid
   b. the dissolution of Ga_2O_3 in concentrated aqueous base
   c. the dissolution of Tl_2O in concentrated aqueous acid
   d. $Ga(l) + S_8(s)$
   e. $Tl(s) + H_2S(g)$

8. Write a balanced chemical equation for the reaction that occurs between Al and each species.
   a. Cl_2
   b. O_2
   c. S
   d. N_2
   e. H_2O
   f. $H^+(aq)$

9. Write a balanced chemical equation that shows how you would prepare each compound from its respective elements or other common compounds.
   a. In_2I_6
   b. $B(OH)_3$
   c. Ga_2O_3
   d. $[Tl(H_2O)_6]^{3+}$
   e. $Al(OH)_4^-$
   f. In_4C_3

10. Write a balanced chemical equation that shows how you would prepare each compound from its respective elements or other common compounds.
   a. BCl_3
   b. $InCl_3$
   c. Tl_2S
   d. $Al(OH)_3$
   e. In_2O_3
   f. AlN

11. Diborane is a spontaneously flammable, toxic gas that is prepared by reacting $NaBH_4$ with BF_3. Write a balanced chemical equation for this reaction.

12. Draw the Lewis electron structure of each reactant and product in each chemical equation. Then describe the type of bonding found in each reactant and product.
   a. $2B(s) + 3X_2(g) \xrightarrow{\Delta} 2BX_3(g)$
   b. $4B(s) + 3O_2(g) \xrightarrow{\Delta} 2B_2O_3(s)$
   c. $2B(s) + N_2(g) \xrightarrow{\Delta} 2BN(s)$

13. Draw the Lewis electron structure of each reactant and product in each chemical equation. Then describe the type of bonding found in each reactant and product.
   a. $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(l)$
   b. $B_2H_6(g) + 6CH_3CH{=}CH_2(g) \rightarrow 2[B(CH_2CH_2CH_3)_3](l)$

Answers

5.

a. $12BCl_3(g) + 18H_2(g) \xrightarrow{\Delta} B_{12}(s) + 36HCl(g)$
b. $6C_2H_4(g) + B_2H_6(g) \rightarrow 2B(C_2H_5)_3(l)$
c. $6B_2H_6(g) + 18Cl_2(g) \rightarrow B_{12}(s) + 36HCl(g)$
d. $B_2H_6(g) + 2(C_2H_5)_2S(g) \rightarrow 2H_3B{\cdot}S(C_2H_5)_2(l)$

7.

a. $Al_2O_3(s) + 6H_3O^+(aq) + 3H_2O(l) \rightarrow 2Al(H_2O)_6{}^{3+}(aq)$
b. $Ga_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Ga(OH)_4{}^-(aq)$
c. $Tl_2O(s) + 2H^+(aq) + 9H_2O(l) \rightarrow 2Tl(H_2O)_6{}^+(aq)$
d. $16Ga(l) + 3S_8(s) \rightarrow 8Ga_2S_3(s)$
e. $2Tl(s) + H_2S(g) \rightarrow Tl_2S(s) + H_2(g)$

9.

a. $2In(s) + 3I_2(s) \xrightarrow{\Delta} In_2I_6(s)$
b. $B_{12}(s) + 18Cl_2(g) \rightarrow 12BCl_3(l)$

$BCl_3(l) + 3H_2O(l) \rightarrow B(OH)_3(aq) + 3HCl(aq)$

c. $4Ga(l) + 3O_2(g) \xrightarrow{\Delta} 2Ga_2O_3(s)$
d. $2Tl(s) + 3Cl_2(g) \rightarrow 2TlCl_3(s)$; $TlCl_3(s) + 6H_2O(l) \rightarrow Tl(H_2O_6)^{3+}(aq) + 3Cl^-(aq)$
e. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$; $2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2Al(OH)_4{}^- + 3H_2(g) + 2Na^+(aq)$
f. $4In(s) + 3C(s) \xrightarrow{\Delta} In_4C_3(s)$

21.5: Group 14: The Carbon Family

Conceptual Problems

1. Why is the preferred oxidation state of lead +2 rather than +4? What do you expect the preferred oxidation state of silicon to be based on its position in the periodic table?
2. Carbon uses pπ–pπ overlap to form compounds with multiple bonds, but silicon does not. Why? How does this same phenomenon explain why the heavier elements in group 14 do not form catenated compounds?
3. Diamond is both an electrical insulator and an excellent thermal conductor. Explain this property in terms of its bonding.
4. The lighter chalcogens (group 16) form π bonds with carbon. Does the strength of these π bonds increase or decrease with increasing atomic number of the chalcogen? Why?
5. The heavier group 14 elements can form complexes that contain expanded coordination spheres. How does this affect their reactivity compared with the reactivity of carbon? Is this a thermodynamic effect or a kinetic effect? Explain your answer.
6. Refer to Table $21.E.1$ for the values of the electron affinities of the group 14 elements. Explain any discrepancies between these actual values and the expected values based on usual periodic trends.
7. Except for carbon, the elements of group 14 can form five or six electron-pair bonds. What hybrid orbitals are used to allow this expanded coordination? Why does carbon not form more than four electron-pair bonds?
8. Which of the group 14 elements is least stable in the +4 oxidation state? Why?

Structure and Reactivity

1. Predict the products of each reaction and balance each chemical equation.
   a. $CaC_2(s) + HCl(g) \rightarrow$
   b. $Pb(s) + Br_2(l) \xrightarrow{\Delta}$
   c. $(CH_3)_3N(l) + H_2O_2(aq) \rightarrow$
   d. $Pb(N_3)_2(s) \xrightarrow{\Delta}$

2. Write a balanced chemical equation to indicate how you would prepare each compound.
   a. $SiF_6{}^{2-}$ from its elements and other common compounds

b. SiO_2 from $SiCl_4$
c. GeS_2 from its elements
d. $Si(CH_3)_4$ from Si

3. Write a balanced chemical equation to indicate how you would prepare each compound.
   a. CO_2 from CuO
   b. methane from Be_2C
   c. $Si(OH)_4$ from Si
   d. Si_3N_4 from Si

Answers

1.

a. $CaC_2(s) + 2HCl(g) \rightarrow CaCl_2(s) + C_2H_2(g)$
b. $Pb(s) + Br_2(l) \xrightarrow{\Delta} PbBr_2(s)$
c. $(CH_3)_3N(l) + H_2O_2(aq) \rightarrow (CH_3)_3N{-}O(l) + H_2O(l)$
d. $Pb(N_3)_2(s) \xrightarrow{\Delta} Pb(s) + 3N_2(g)$

3.

a. $CuO(s) + CO(s) \xrightarrow{\Delta} Cu(s) + CO_2(g)$
b. $Be_2C(s) + 4HCl(aq) \rightarrow 2BeCl_2(aq) + CH_4(g)$
c. $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$; $SiCl_4(l) + 4H_2O(l) \rightarrow Si(OH)_4(s) + 4HCl(aq)$
d. $3Si(s) + 2N_2(g) \xrightarrow{\Delta} Si_3N_4(s)$

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22: CHEMISTRY OF THE MAIN-GROUP ELEMENTS II

Petrucci: *General Chemistry*
Principles and Modern Applications

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22.1: Periodic Trends in Bonding

Periodic trends affect bonding, because of how the elements are arranged on the periodic table. For example elements can be arranged by their electronegative, electron affinity, atomic radius, or ionization energy. Electronegative is the atoms ability to attract other bonded atoms. Electron affinity is an atoms ability to attract another atom. The atomic radius is the radius of an elements atom. Ionization energy is the energy it takes to remove an atom from another atom. Other periodic trends are when the attraction of the atoms for the pair of bonding electrons is different, this is polar covalent bonds. Properties in compounds are used to determine the type of bonding and structure, not just the elements being used. These different properties help group elements to make them either more available or less available for bonding.

Fluorides

It may seem counterintuitive to say that HF is the weakest hydrohalic acid because fluorine has the highest electronegativity. However, the H-F bond is very strong; if the H-X bond is strong, the resulting acid is weak. A strong bond is determined by a short bond length and a large bond dissociation energy. Of all the hydrogen halides, HF has the shortest bond length and largest bond dissociation energy.

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 22.1.1) 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 22.1.1*: 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.*

Oxides

Oxides are binary compounds of oxygen with another element, e.g., CO_2, SO_2, CaO, CO, ZnO, BaO_2, H_2O, etc. These are termed as oxides because here, oxygen is in combination with only one element. Based on their acid-base characteristics oxides are classified as acidic, basic, amphoteric or neural:

1. An oxide that combines with water to give an acid is termed as an acidic oxide.

2. The oxide that gives a base in water is known as a basic oxide.
3. An amphoteric solution is a substance that can chemically react as either acid or base.
4. However, it is also possible for an oxide to be neither acidic nor basic, but is a neutral oxide.

There are different properties which help distinguish between the three types of oxides. The term **anhydride** ("without water") refers to compounds that assimilate H_2O to form either an acid or a base upon the addition of water.

Acidic Oxides

Acidic oxides are the oxides of non-metals (Groups 14-17) and these **acid anhydrides** form acids with water:

- Sulfurous Acid

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{22.1.1}$$

- Sulfuric Acid

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{22.1.2}$$

- Carbonic Acid

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{22.1.3}$$

Acidic oxides are known as acid anhydrides (e.g., sulfur dioxide is sulfurous anhydride and sulfur trioxide is sulfuric anhydride) and when combined with bases, they produce salts, e.g.,

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O \tag{22.1.4}$$

Basic Oxides

Generally Group 1 and Group 2 elements form bases called base anhydrides or basic oxides, e.g.,

$$K_2O\ (s) + H_2O\ (l) \rightarrow 2KOH\ (aq) \tag{22.1.5}$$

Basic oxides are the oxides of metals. If soluble in water, they react with water to produce hydroxides (alkalies) e.g.,

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{22.1.6}$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \tag{22.1.7}$$

$$Na_2O + H_2O \rightarrow 2NaOH \tag{22.1.8}$$

These metallic oxides are known as basic anhydrides. They react with acids to produce salts, e.g.,

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O \tag{22.1.9}$$

$$Na_2O + H_2SO_4 \rightarrow Na_2SO_4 + H_2O \tag{22.1.10}$$

Amphoteric Oxides

An amphoteric solution is a substance that can chemically react as either acid or base. For example, when HSO_4^- reacts with water it will make both hydroxide and hydronium ions:

$$HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+ \tag{22.1.11}$$

$$HSO_4^- + H_2O \rightarrow H_2SO_4 + OH^- \tag{22.1.12}$$

Amphoteric oxides are metallic oxides, which show both basic as well as acidic properties. When they react with an acid, they produce salt and water, showing basic properties. While reacting with alkalies they form salt and water showing acidic properties, e.g.,

$$ZnO + 2HCl \rightarrow \underset{zinc\ chloride}{ZnCl_2} + H_2O\,(basic\ nature) \tag{22.1.13}$$

$$ZnO + 2NaOH \rightarrow \underset{sodium\ zincate}{Na_2ZnO_2} + H_2O\,(acidic\ nature) \tag{22.1.14}$$

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O\,(basic\ nature) \tag{22.1.15}$$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O\,(acidic\ nature) \tag{22.1.16}$$

Amphoteric oxides have both acidic and basic properties. A common example of an amphoteric oxide is aluminum oxide. In general, amphoteric oxides form with metalloids. (see chart below for more detail). Example with acidic properties:

$$Al_2O_3 + H_2O \rightarrow 2Al(OH) + 2H^+ \tag{22.1.17}$$

Example with basic properties:

$$Al_2O_3 + H_2O \rightarrow 2Al^{3+} + 3OH^- \tag{22.1.18}$$

Neutral Oxides

Neutral oxides show neither basic nor acidic properties and hence do not form salts when reacted with acids or bases, e.g., carbon monoxide (CO); nitrous oxide (N_2O); nitric oxide (NO), etc., are neutral oxides.

Peroxides and Dioxides

Oxides: Group 1 metals react rapidly with oxygen to produce several different ionic oxides, usually in the form of M_2O. With the oyxgen exhibiting an oxidation number of -2.

$$4Li + O_2 \rightarrow 2Li_2O \tag{22.1.19}$$

Peroxides: Often Lithium and Sodium reacts with **excess** oxygen to produce the peroxide, M_2O_2. with the oxidation number of the oxygen equal to -1.

$$H_2 + O_2 \rightarrow H_2O_2 \tag{22.1.20}$$

Superoxides: Often Potassium, Rubidium, and Cesium react with excess oxygen to produce the superoxide, MO_2. with the oxidation number of the oxygen equal to -1/2.

$$Cs + O_2 \rightarrow CsO_2 \tag{22.1.21}$$

A peroxide is a metallic oxide which gives hydrogen peroxide by the action of dilute acids. They contain more oxygen than the corresponding basic oxide, e.g., sodium, calcium and barium peroxides.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2 \tag{22.1.22}$$

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2 \tag{22.1.23}$$

Dioxides like PbO_2 and MnO_2 also contain higher percentage of oxygen like peroxides and have similar molecular formulae. These oxides, however, do not give hydrogen peroxide by action with dilute acids. Dioxides on reaction with concentrated HCl yield Cl_2 and on reacting with concentrated H_2SO_4 yield O_2.

$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O \tag{22.1.24}$$

$$2PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O + O_2 \tag{22.1.25}$$

Compound Oxides

Compound oxides are metallic oxides that behave as if they are made up of two oxides, one that has a lower oxidation and one with a higher oxidation of the same metal, e.g.,

$$\text{Red lead: } Pb_3O_4 = PbO_2 + 2PbO \tag{22.1.26}$$

$$\text{Ferro-ferric oxide: } Fe_3O_4 = Fe_2O_3 + FeO \tag{22.1.27}$$

On treatment with an acid, compound oxides give a mixture of salts.

$$\underset{\text{Ferro-ferric oxide}}{Fe_3O_4} + 8HCl \rightarrow \underset{\text{ferric chloride}}{2FeCl_3} + \underset{\text{ferrous chloride}}{FeCl_2} + 4H_2O \tag{22.1.28}$$

Preparation of Oxides

Oxides can be generated via multiple reactions. Below are a few.

By direct heating of an element with oxygen: Many metals and non-metals burn rapidly when heated in oxygen or air, producing their oxides, e.g.,

$$2Mg + O_2 \xrightarrow{Heat} 2MgO \tag{22.1.29}$$

$$2Ca + O_2 \xrightarrow{Heat} 2CaO \tag{22.1.30}$$

$$S + O_2 \xrightarrow{Heat} SO_2 \tag{22.1.31}$$

$$P_4 + 5O_2 \xrightarrow{Heat} 2P_2O_5 \tag{22.1.32}$$

By reaction of oxygen with compounds at higher temperatures: At higher temperatures, oxygen also reacts with many compounds forming oxides, e.g.,

- sulfides are usually oxidized when heated with oxygen.

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2 \tag{22.1.33}$$

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2 \tag{22.1.34}$$

- When heated with oxygen, compounds containing carbon and hydrogen are oxidized.

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \tag{22.1.35}$$

- By thermal decomposition of certain compounds like hydroxides, carbonates, and nitrates

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \tag{22.1.36}$$

$$2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2 \tag{22.1.37}$$

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O \tag{22.1.38}$$

By oxidation of some metals with nitric acid

$$2Cu + 8HNO_3 \xrightarrow{Heat} 2CuO + 8NO_2 + 4H_2O + O_2 \tag{22.1.39}$$

$$Sn + 4HNO_3 \xrightarrow{Heat} SnO_2 + 4NO_2 + 2H_2O \tag{22.1.40}$$

By oxidation of some non-metals with nitric acid

$$C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O \tag{22.1.41}$$

Trends in Acid-Base Behavior

The oxides of elements in a period become progressively more acidic as one goes from left to right in a period of the periodic table. For example, in third period, the behavior of oxides changes as follows:

$$\underbrace{Na_2O,\ MgO}_{Basic} \quad \underbrace{Al_2O_3,\ SiO_2}_{Amphoteric} \quad \underbrace{P_4O_{10},\ SO_3,\ Cl_2O_7}_{Acidic} \tag{22.1.42}$$

If we take a closer look at a specific period, we may better understand the acid-base properties of oxides. It may also help to examine the physical properties of oxides, but it is not necessary (Table 22.1.1). Metal oxides on the left side of the periodic table produce basic solutions in water (e.g. Na_2O and MgO). Non-metal oxides on the right side of the periodic table produce acidic solutions (e.g. Cl_2O, SO_2, P_4O_{10}). There is a trend within acid-base behavior: basic oxides are present on the left side of the period and acidic oxides are found on the right side.

Table 22.1.1: Oxides of the s- and p-block elements.basic oxides (purple), amphoteric oxides (blue), and acidic oxides (red)

1	2	3	14	15	16	17
Li	Be	B	**C**	**N**	**O**	**F**
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**
Cs	**Ba**	**Tl**	**Pb**	**Bi**	**Po**	**At**

Aluminum oxide shows acid and basic properties of an oxide, it is amphoteric. Thus Al_2O_3 entails the marking point at which a change over from a basic oxide to acidic oxide occurs. It is important to remember that the trend only applies for oxides in their highest oxidation states. The individual element must be in its highest possible oxidation state because the trend does not follow if all oxidation states are included. Notice how the amphoteric oxides (shown in blue) of each period signify the change from basic to acidic oxides.

Contributors and Attributions

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22.2: Group 18 - The 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 22.2.1 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 22.2.1: 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 22.2.5.	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 22.2.1).

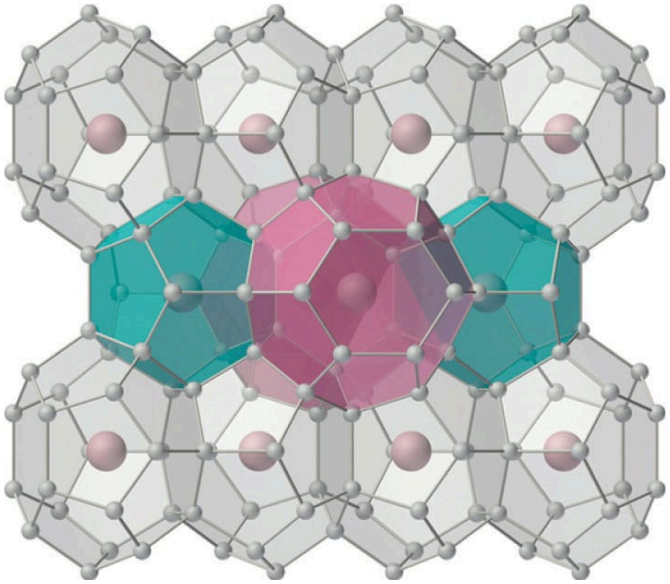


Figure 22.2.1: The Structure of Xenon Hydrate, a Clathrate. Small gaseous atoms or molecules such as Xe or CH_4 can occupy cavities in a lattice of hydrogen-bonded water molecules to produce a stable structure with a fixed stoichiometry (in this case, $Xe{\cdot}5.75H_2O$). (The hydrogen atoms of the 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 22.2.2: “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 22.2.3). 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:

$$\mathrm{Xe\,(g) + PtF_6\,(g) \longrightarrow [XeF^{+}][PtF_5{}^{-}]\,(s)} \tag{22.2.1}$$

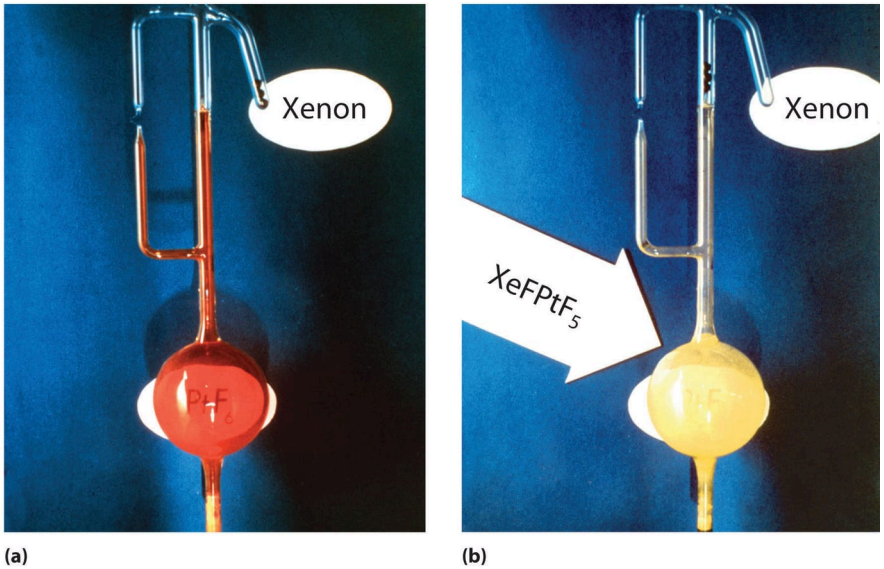


Figure 22.2.3: The Synthesis of the First Chemical Compound of Xenon. (a) An apparatus containing platinum hexafluoride, the red vapor at the bottom left, and xenon, the colorless gas in the small tube at the upper right. (b) When the glass seal separating the two gases is broken and the gases are allowed 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:

$$\mathrm{Xe\,(g) + 2\,F_2\,(g) \longrightarrow XeF_4\,(s)} \tag{22.2.2}$$

The ionization energies of helium, neon, and argon are so high (Table 22.2.1) 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.

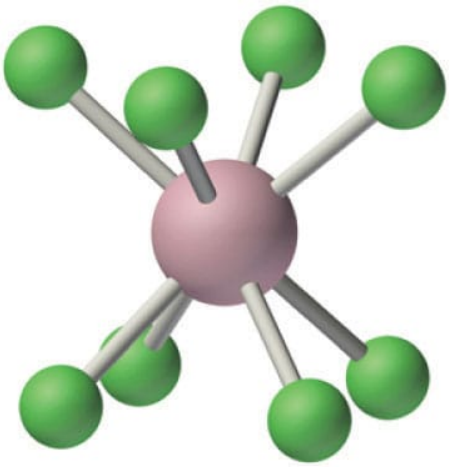
The ionization energies of helium, neon, and argon are so high that no stable compounds of these elements are known.

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:

$$\mathrm{XeF_6\,(s) + CsF\,(s) \longrightarrow CsXeF_7\,(s)} \tag{22.2.3}$$

$$\mathrm{2\,CsXeF_7\,(s) \xrightarrow{\Delta} Cs_2XeF_8\,(s) + XeF_6\,(g)} \tag{22.2.4}$$

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:

$$\mathrm{XeF_6\,(aq) + 3\,H_2O\,(l) \longrightarrow XeO_3\,(aq) + 6\,HF\,(aq)} \tag{22.2.5}$$

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 22.2.1

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 22.2.1

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 22.2.1

$KXeF_7$; 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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22.3: Group 17: The Halogens

Learning Objectives

- To understand the periodic trends and reactivity of the group 17 elements: the halogens.

Because the halogens are highly reactive, none is found in nature as the free element. Hydrochloric acid, which is a component of aqua regia (a mixture of HCl and HNO_3 that dissolves gold), and the mineral fluorspar (CaF_2) were well known to alchemists, who used them in their quest for gold. Despite their presence in familiar substances, none of the halogens was even recognized as an element until the 19th century.

Because the halogens are highly reactive, none is found in nature as the free element.

Chlorine was the first halogen to be obtained in pure form. In 1774, Carl Wilhelm Scheele (the codiscoverer of oxygen) produced chlorine by reacting hydrochloric acid with manganese dioxide. Scheele was convinced, however, that the pale green gas he collected over water was a compound of oxygen and hydrochloric acid. In 1811, Scheele's "compound" was identified as a new element, named from the Greek chloros, meaning "yellowish green" (the same stem as in chlorophyll, the green pigment in plants). That same year, a French industrial chemist, Bernard Courtois, accidentally added too much sulfuric acid to the residue obtained from burned seaweed. A deep purple vapor was released, which had a biting aroma similar to that of Scheele's "compound." The purple substance was identified as a new element, named iodine from the Greek iodes, meaning "violet." Bromine was discovered soon after by a young French chemist, Antoine Jérôme Balard, who isolated a deep red liquid with a strong chlorine-like odor from brine from the salt marshes near Montpellier in southern France. Because many of its properties were intermediate between those of chlorine and iodine, Balard initially thought he had isolated a compound of the two (perhaps ICl). He soon realized, however, that he had discovered a new element, which he named bromine from the Greek bromos, meaning "stench." Currently, organic chlorine compounds, such as PVC (polyvinylchloride), consume about 70% of the Cl_2 produced annually; organobromine compounds are used in much smaller quantities, primarily as fire retardants.



A crystal of the mineral fluorite (CaF_2). The purple color of some fluorite crystals is due to small inclusions of highly oxidizing impurities, which generate detectable amounts of ozone when the crystals are crushed.

Because of the unique properties of its compounds, fluorine was believed to exist long before it was actually isolated. The mineral fluorspar (now called fluorite [CaF_2]) had been used since the 16th century as a "flux," a low-melting-point substance that could dissolve other minerals and ores. In 1670, a German glass cutter discovered that heating fluorspar with strong acid produced a solution that could etch glass. The solution was later recognized to contain the acid of a new element, which was named fluorine in 1812. Elemental fluorine proved to be very difficult to isolate, however, because both HF and F_2 are extraordinarily reactive and

toxic. After being poisoned three times while trying to isolate the element, the French chemist Henri Moissan succeeded in 1886 in electrolyzing a sample of KF in anhydrous HF to produce a pale green gas (Figure 22.3.1). For this achievement, among others, Moissan narrowly defeated Mendeleev for the Nobel Prize in Chemistry in 1906. Large amounts of fluorine are now consumed in the production of cryolite (Na_3AlF_6), a key intermediate in the production of aluminum metal. Fluorine is also found in teeth as fluoroapatite [$Ca_5(PO_4)_3F$], which is formed by reacting hydroxyapatite [$Ca_5(PO_4)_3OH$] in tooth enamel with fluoride ions in toothpastes, rinses, and drinking water.



Figure 22.3.1 Isolation of Elemental Fluorine. The French chemist Henri Moissan was the first person to isolate elemental fluorine. A reproduction of the U-shaped electrolysis cell with which Moissan first isolated elemental fluorine in 1866 is shown with samples of cryolite (left) and fluorspar (right). Fluorspar is the raw material from which anhydrous hydrofluoric acid (HF) is prepared. Cryolite is a rare mineral that contains the fluoride ion.

The heaviest halogen is astatine (At), which is continuously produced by natural radioactive decay. All its isotopes are highly radioactive, and the most stable has a half-life of only about 8 h. Consequently, astatine is the least abundant naturally occurring element on Earth, with less than 30 g estimated to be present in Earth's crust at any one time.

Preparation and General Properties of the Group 17 Elements

All the halogens except iodine are found in nature as salts of the halide ions (X^-), so the methods used for preparing F_2, Cl_2, and Br_2 all involve oxidizing the halide. Reacting CaF_2 with concentrated sulfuric acid produces gaseous hydrogen fluoride:

$$CaF_{2(s)} + H_2SO_{4(l)} \rightarrow CaSO_{4(s)} + 2HF_{(g)} \tag{22.3.1}$$

Fluorine is produced by the electrolysis of a 1:1 mixture of HF and $K^+HF_2^-$ at 60–300°C in an apparatus made of Monel, a highly corrosion-resistant nickel–copper alloy:

$$KHF_2 \cdot HF(l) \xrightarrow{electrolysis} F_2(g) + H_2(g) \tag{22.3.2}$$

Fluorine is one of the most powerful oxidants known, and both F_2 and HF are highly corrosive. Consequently, the production, storage, shipping, and handling of these gases pose major technical challenges.

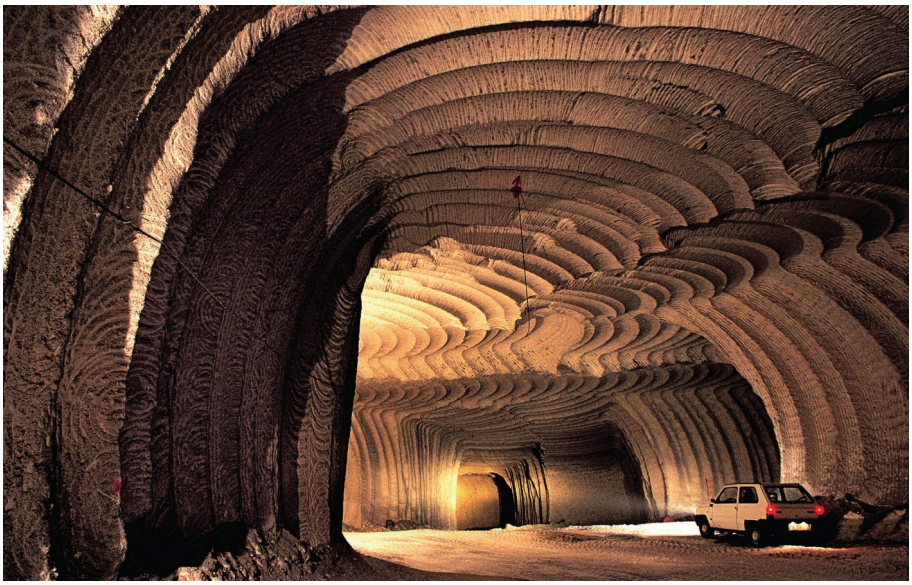


Figure 22.3.2: A Subterranean Salt Mine. Subterranean deposits of rock salt are located worldwide, such as this one at Petralia in Sicily.

Although chlorine is significantly less abundant than fluorine, elemental chlorine is produced on an enormous scale. Fortunately, large subterranean deposits of rock salt (NaCl) are found around the world (Figure 22.3.2), and seawater consists of about 2% NaCl by mass, providing an almost inexhaustible reserve. Inland salt lakes such as the Dead Sea and the Great Salt Lake are even richer sources, containing about 23% and 8% NaCl by mass, respectively. Chlorine is prepared industrially by the chloralkali process, which uses the following reaction:

$$2NaCl_{(aq)} + 2H_2O_{(l)} \xrightarrow{electrolysis} 2NaOH(aq) + Cl_{2(g)} + H_{2(g)} \tag{22.3.3}$$

Bromine is much less abundant than fluorine or chlorine, but it is easily recovered from seawater, which contains about 65 mg of Br^- per liter. Salt lakes and underground brines are even richer sources; for example, the Dead Sea contains 4 g of Br^- per liter. Iodine is the least abundant of the nonradioactive halogens, and it is a relatively rare element. Because of its low electronegativity, iodine tends to occur in nature in an oxidized form. Hence most commercially important deposits of iodine, such as those in the Chilean desert, are iodate salts such as $Ca(IO_3)_2$. The production of iodine from such deposits therefore requires reduction rather than oxidation. The process is typically carried out in two steps: reduction of iodate to iodide with sodium hydrogen sulfite, followed by reaction of iodide with additional iodate:

$$2IO^-_{3(aq)} + 6HSO^-_{3(aq)} \rightarrow 2I^-_{(aq)} + 6SO^2{}_{-4(aq)} + 6H^+_{(aq)} \tag{22.3.4}$$

$$5I^-_{(aq)} + IO^-_{3(aq)} + 6H^+_{(aq)} \rightarrow 3I_{2(s)} + 3H_2O_{(l)} \tag{22.3.5}$$

Because the halogens all have ns^2np^5 electron configurations, their chemistry is dominated by a tendency to accept an additional electron to form the closed-shell ion (X^-). Only the electron affinity and the bond dissociation energy of fluorine differ significantly from the expected periodic trends shown in Table 22.3.1. Electron–electron repulsion is important in fluorine because of its small atomic volume, making the electron affinity of fluorine less than that of chlorine. Similarly, repulsions between electron pairs on adjacent atoms are responsible for the unexpectedly low F–F bond dissociation energy. (As discussed earlier, this effect is also responsible for the weakness of O–O, N–N, and N–O bonds.)

> Electrostatic repulsions between lone pairs of electrons on adjacent atoms cause single bonds between N, O, and F to be weaker than expected.

Table 22.3.1: Selected Properties of the Group 17 Elements

Property	Fluorine	Chlorine	Bromine	Iodine	Astatine
atomic symbol	F	Cl	Br	I	At
***The configuration shown does not include filled d and f subshells. †The values cited are for the six-coordinate anion (X^-).**					

Property	Fluorine	Chlorine	Bromine	Iodine	Astatine
atomic number	9	17	35	53	85
atomic mass (amu)	19.00	35.45	79.90	126.90	210
valence electron configuration*	$2s^2 2p^5$	$3s^2 3p^5$	$4s^2 4p^5$	$5s^2 5p^5$	$6s^2 6p^5$
melting point/boiling point (°C)	−220/−188	−102/−34.0	−7.2/58.8	114/184	302/—
density (g/cm^3) at 25°C	1.55 (g/L)	2.90 (g/L)	3.10	4.93	—
atomic radius (pm)	42	79	94	115	127
first ionization energy (kJ/mol)	1681	1251	1140	1008	926
normal oxidation state(s)	−1	−1 (+1, +3, +5, +7)	−1 (+1, +3, +5, +7)	−1 (+1, +3, +5, +7)	−1, +1
ionic radius (pm)†	133	181	196	220	—
electron affinity (kJ/mol)	−328	−349	−325	−295	−270
electronegativity	4.0	3.2	3.0	2.7	2.2
standard reduction potential (E°, V) ($X_2 \rightarrow X^-$ in basic solution)	+2.87	+1.36	+1.07	+0.54	+0.30
dissociation energy of X_2(g) (kJ/mol)	158.8	243.6	192.8	151.1	~80
product of reaction with O_2	O_2F_2	none	none	none	none
type of oxide	acidic	acidic	acidic	acidic	acidic
product of reaction with N_2	none	none	none	none	none
product of reaction with H_2	HF	HCl	HBr	HI	HAt

***The configuration shown does not include filled d and f subshells. †The values cited are for the six-coordinate anion (X^-).**

Because it is the most electronegative element in the periodic table, fluorine forms compounds in only the −1 oxidation state. Notice, however, that all the halogens except astatine have electronegativities greater than 2.5, making their chemistry exclusively that of nonmetals. The halogens all have relatively high ionization energies, but the energy required to remove electrons decreases substantially as we go down the column. Hence the heavier halogens also form compounds in positive oxidation states (+1, +3, +5, and +7), derived by the formal loss of ns and np electrons.

> Because ionization energies decrease down the group, the heavier halogens form compounds in positive oxidation states (+1, +3, +5, and +7).

Reactions and Compounds of the Halogens

Fluorine is the most reactive element in the periodic table, forming compounds with every other element except helium, neon, and argon. The reactions of fluorine with most other elements range from vigorous to explosive; only O_2, N_2, and Kr react slowly. There are three reasons for the high reactivity of fluorine:

1. Because fluorine is so electronegative, it is able to remove or at least share the valence electrons of virtually any other element.
2. Because of its small size, fluorine tends to form very strong bonds with other elements, making its compounds thermodynamically stable.
3. The F–F bond is weak due to repulsion between lone pairs of electrons on adjacent atoms, reducing both the thermodynamic and kinetic barriers to reaction.

With highly electropositive elements, fluorine forms ionic compounds that contain the closed-shell F^- ion. In contrast, with less

electropositive elements (or with metals in very high oxidation states), fluorine forms covalent compounds that contain terminal F atoms, such as SF_6. Because of its high electronegativity and $2s^2 2p^5$ valence electron configuration, fluorine normally participates in only one electron-pair bond. Only a very strong Lewis acid, such as AlF_3, can share a lone pair of electrons with a fluoride ion, forming AlF_6^{3-}.

Oxidative strength decreases down group 17.

The halogens (X_2) react with metals (M) according to the general equation

$$M_{(s,l)} + nX_{2(s,l,g)} \rightarrow MX_{n(s,l)} \tag{22.3.6}$$

For elements that exhibit multiple oxidation states fluorine tends to produce the highest possible oxidation state and iodine the lowest. For example, vanadium reacts with the halogens to give VF_5, VCl_4, VBr_4, and VI_3.

Metal halides in the +1 or +2 oxidation state, such as CaF_2, are typically ionic halides, which have high melting points and are often soluble in water. As the oxidation state of the metal increases, so does the covalent character of the halide due to polarization of the M–X bond. With its high electronegativity, fluoride is the least polarizable, and iodide, with the lowest electronegativity, is the most polarizable of the halogens. Halides of small trivalent metal ions such as Al^{3+} tend to be relatively covalent. For example, $AlBr_3$ is a volatile solid that contains bromide-bridged Al_2Br_6 molecules. In contrast, the halides of larger trivalent metals, such as the lanthanides, are essentially ionic. For example, indium tribromide ($InBr_3$) and lanthanide tribromide ($LnBr_3$) are all high-melting-point solids that are quite soluble in water.

As the oxidation state of the metal increases, the covalent character of the corresponding metal halides also increases due to polarization of the M–X bond.

All halogens react vigorously with hydrogen to give the hydrogen halides (HX). Because the H–F bond in HF is highly polarized ($H^{\delta+}$–$F^{\delta-}$), liquid HF has extensive hydrogen bonds, giving it an unusually high boiling point and a high dielectric constant. As a result, liquid HF is a polar solvent that is similar in some ways to water and liquid ammonia; after a reaction, the products can be recovered simply by evaporating the HF solvent. (Hydrogen fluoride must be handled with extreme caution, however, because contact of HF with skin causes extraordinarily painful burns that are slow to heal.) Because fluoride has a high affinity for silicon, aqueous hydrofluoric acid is used to etch glass, dissolving SiO_2 to give solutions of the stable SiF_6^{2-} ion.



Glass etched with hydrogen flouride. *© Thinkstock*

Except for fluorine, all the halogens react with water in a disproportionation reaction, where X is Cl, Br, or I:

$$X_{2(g,l,s)} + H_2O_{(l)} \rightarrow H^+_{(aq)} + X^-_{(aq)} + HOX_{(aq)} \tag{22.3.7}$$

The most stable oxoacids are the perhalic acids, which contain the halogens in their highest oxidation state (+7). The acid strengths of the oxoacids of the halogens increase with increasing oxidation state, whereas their stability and acid strength decrease down the group. Thus perchloric acid ($HOClO_3$, usually written as $HClO_4$) is a more potent acid and stronger oxidant than perbromic acid. Although all the oxoacids are strong oxidants, some, such as $HClO_4$, react rather slowly at low temperatures. Consequently, mixtures of the halogen oxoacids or oxoanions with organic compounds are potentially explosive if they are heated or even agitated mechanically to initiate the reaction. Because of the danger of explosions, oxoacids and oxoanions of the halogens should never be allowed to come into contact with organic compounds.

Both the acid strength and the oxidizing power of the halogen oxoacids decrease down the group.

The halogens react with one another to produce interhalogen compounds, such as ICl_3, BrF_5, and IF_7. In all cases, the heavier halogen, which has the lower electronegativity, is the central atom. The maximum oxidation state and the number of terminal halogens increase smoothly as the ionization energy of the central halogen decreases and the electronegativity of the terminal halogen increases. Thus depending on conditions, iodine reacts with the other halogens to form IF_n (n = 1–7), ICl or ICl_3, or IBr, whereas bromine reacts with fluorine to form only BrF, BrF_3, and BrF_5 but not BrF_7. The interhalogen compounds are among the most powerful Lewis acids known, with a strong tendency to react with halide ions to give complexes with higher coordination numbers, such as the IF_8^- ion:

$$IF_{7(l)} + KF_{(s)} \rightarrow KIF_{8(s)} \tag{22.3.8}$$

All group 17 elements form compounds in odd oxidation states (–1, +1, +3, +5, +7). The interhalogen compounds are also potent oxidants and strong fluorinating agents; contact with organic materials or water can result in an explosion.

All group 17 elements form compounds in odd oxidation states (–1, +1, +3, +5, +7), but the importance of the higher oxidation states generally decreases down the group.

Example 22.3.1

For each reaction, explain why the given products form.

a. $ClF_3(g) + Cl_2(g) \rightarrow 3ClF(g)$
b. $2KI(s) + 3H_2SO_4(aq) \rightarrow I_2(aq) + SO_2(g) + 2KHSO_4(aq) + 2H_2O(l)$
c. $Pb(s) + 2BrF_3(l) \rightarrow PbF_4(s) + 2BrF(g)$

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. When the reactants have the same element in two different oxidation states, we expect the product to have that element in an intermediate oxidation state. We have Cl^{3+} and Cl^0 as reactants, so a possible product would have Cl in either the +1 or +2 oxidation state. From our discussion, we know that +1 is much more likely. In this case, Cl_2 is behaving like a reductant rather than an oxidant.
b. At first glance, this appears to be a simple acid–base reaction, in which sulfuric acid transfers a proton to I^- to form HI. Recall, however, that I^- can be oxidized to I_2. Sulfuric acid contains sulfur in its highest oxidation state (+6), so it is a good oxidant. In this case, the redox reaction predominates.
c. This is the reaction of a metallic element with a very strong oxidant. Consequently, a redox reaction will occur. The only question is whether lead will be oxidized to Pb(II) or Pb(IV). Because BrF_3 is a powerful oxidant and fluorine is able to stabilize high oxidation states of other elements, it is likely that PbF_4 will be the product. The two possible reduction

products for BrF_3 are BrF and Br_2. The actual product will likely depend on the ratio of the reactants used. With excess BrF_3, we expect the more oxidized product (BrF). With lower ratios of oxidant to lead, we would probably obtain Br_2 as the product.

Exercise 22.3.1

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $CaCl_2(s) + H_3PO_4(l) \rightarrow$
b. $GeO_2(s) + HF(aq) \rightarrow$
c. $Fe_2O_3(s) + HCl(g) \xrightarrow{\Delta}$
d. $NaClO_2(aq) + Cl_2(g) \rightarrow$

Answer

a. $CaCl_2(s) + H_3PO_4(l) \rightarrow 2HCl(g) + Ca(HPO_4)(soln)$
b. $GeO_2(s) + 6HF(aq) \rightarrow GeF_6^{2-}(aq) + 2H_2O(l) + 2H^+(aq)$
c. $Fe_2O_3(s) + 6HCl(g) \xrightarrow{\Delta} 2FeCl_3(s) + 3H_2O(g)$
d. $2NaClO_2(aq) + Cl_2(g) \rightarrow 2ClO_2(g) + 2NaCl(aq)$

Summary

The halogens are highly reactive. All halogens have relatively high ionization energies, and the acid strength and oxidizing power of their oxoacids decreases down the group. The halogens are so reactive that none is found in nature as the free element; instead, all but iodine are found as halide salts with the X^- ion. Their chemistry is exclusively that of nonmetals. Consistent with periodic trends, ionization energies decrease down the group. Fluorine, the most reactive element in the periodic table, has a low F–F bond dissociation energy due to repulsions between lone pairs of electrons on adjacent atoms. Fluorine forms ionic compounds with electropositive elements and covalent compounds with less electropositive elements and metals in high oxidation states. All the halogens react with hydrogen to produce hydrogen halides. Except for F_2, all react with water to form oxoacids, including the perhalic acids, which contain the halogens in their highest oxidation state. Halogens also form interhalogen compounds; the heavier halogen, with the lower electronegativity, is the central atom.

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22.4: Group 16: The Oxygen Family

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 22.4.1: 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).

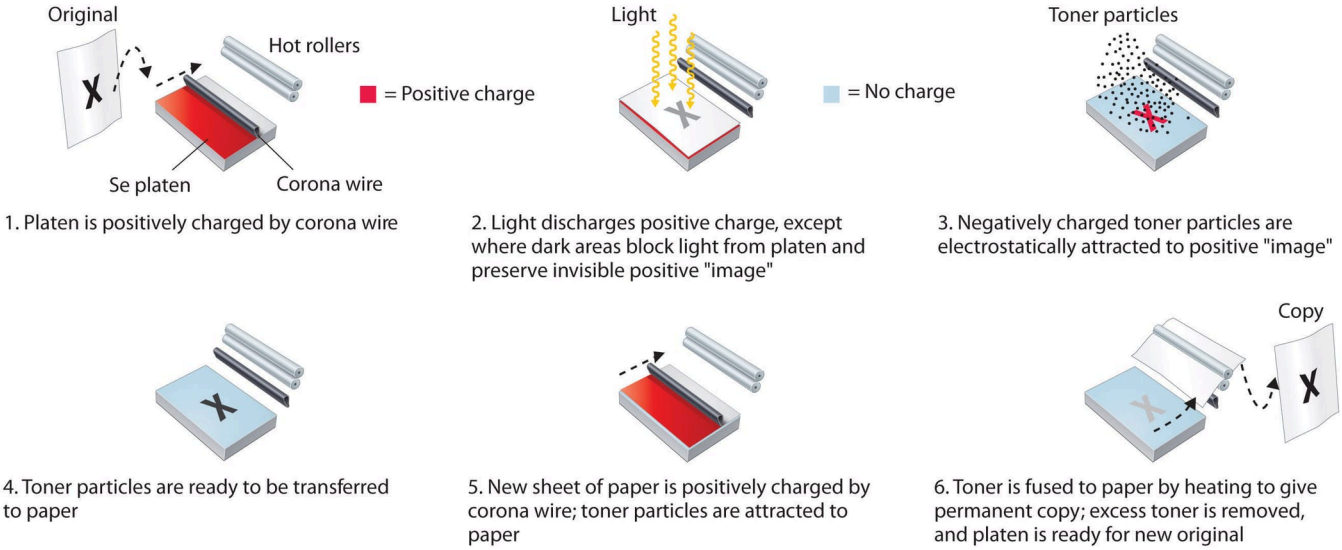


Figure 22.4.1: The Chemistry of Photocopying. Because amorphous selenium is a photosensitive semiconductor, exposing an electrostatically charged Se film to light causes the positive charge on the film to be discharged in all areas that are white in the original. Dark areas in the original block the 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:

$$2\mathrm{KClO_3(s)} \overset{\underset{\Delta}{\mathrm{MnO_2(s)}}}{\rightleftharpoons} 2\mathrm{KCl(s)} + 3\mathrm{O_2(g)} \tag{22.4.1}$$

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 22.4.1). 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 22.4.1. 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 22.4.1: 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:

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)} \qquad \Delta G^o = -119\ kJ/mol \tag{22.4.2}$$

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 22.4.2. 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 22.4.2: 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:

$$H_2O_{(l)} + SO_{3(g)} \rightarrow H_2SO_{4(aq)} \tag{22.4.3}$$

The oxides of the semimetals and of elements such as Al that lie near the metal/nonmetal dividing line are amphoteric, as we expect:

$$Al_2O_{3(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)} \tag{22.4.4}$$

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} \tag{22.4.5}$$

> 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 22.4.1

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 22.4.5).
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 22.4.2

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 22.4.2), 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.

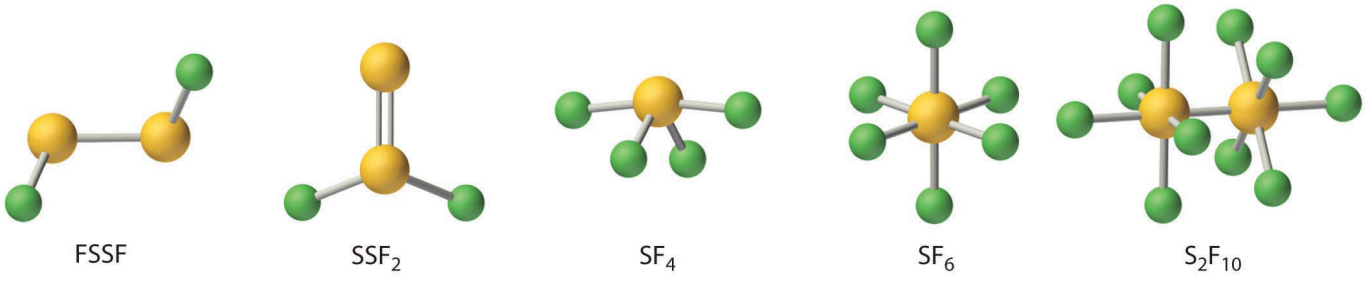


Figure 22.4.2: The Structures of the Known Fluorides of Sulfur. Five stable sulfur fluorides are known, containing sulfur in oxidation states ranging from +1 to +6. All are volatile molecular compounds that vary tremendously in stability and toxicity. Although both SF_6 and S_2F_{10} are very stable, 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 22.4.2). 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 22.4.2

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

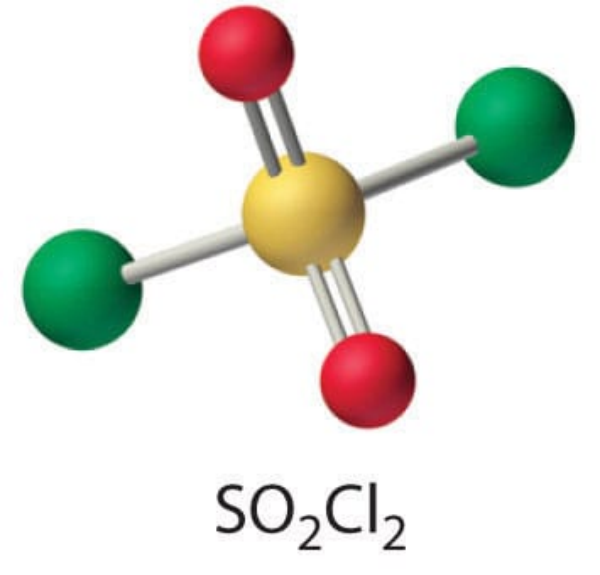
Asked for: why the given products (or no products) form

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 22.4.2

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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22.5: Group 15: The Nitrogen Family

Learning Objectives

- To understand the trends in properties and reactivity of the group 15 elements: the pnicogens.

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. 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 22.5.1). 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 22.5.1: 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.

Although nitrogen is the most abundant element in the atmosphere, it was the last of the pnicogens 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 the Group 15 Elements

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:

$$2\mathrm{NaN_3(s)} \xrightarrow{\Delta} 2\mathrm{Na(l)} + 3\mathrm{N_2(g)} \tag{22.5.1}$$

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.

The other three pnicogens are much less abundant: 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 22.5.1). 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 22.5.1: 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

***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 $H_3EO_4 + 2H^+ + 2e^- \longrightarrow H_3EO_3 + H_2O$; and for Sb it is $Sb_2O_5 + 4e^- + 10H^+ \longrightarrow 2Sb^{3+} + 5H_2O$.**

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
atomic mass (amu)	14.01	30.97	74.92	121.76	209.98
valence electron configuration*	$2s^2 2p^3$	$3s^2 3p^3$	$4s^2 4p^3$	$5s^2 5p^3$	$6s^2 6p^3$
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
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 $H_3EO_4 + 2H^+ + 2e^- \longrightarrow H_3EO_3 + H_2O$; and for Sb it is $Sb_2O_5 + 4e^- + 10H^+ \longrightarrow 2Sb^{3+} + 5H_2O$.**

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.

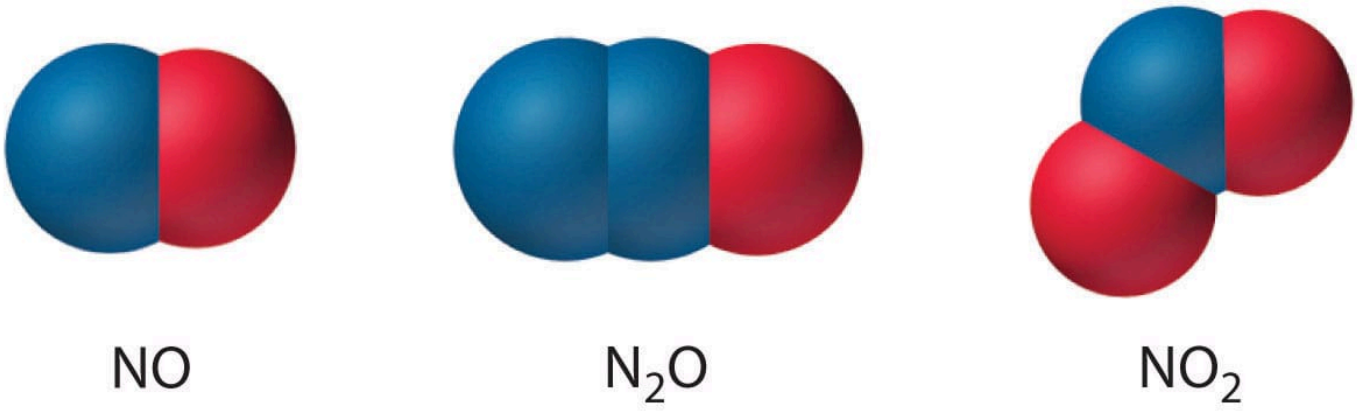
Reactions and Compounds of Nitrogen

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):

$$2\,NO_2\,(g) + H_2O\,(l) \rightarrow HNO_2\,(aq) + HNO_3\,(aq) \tag{22.5.2}$$

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:

$$4\,NH_3\,(g) + 3\,O_2\,(g) \rightarrow 2\,N_2\,(g) + 6\,H_2O\,(g) \tag{22.5.3}$$

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 22.5.1

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. $NH_4NO_2(s) \xrightarrow{\Delta} N_2(g) + 2H_2O(g)$
c. $Pb(NO_3)_2(s) \xrightarrow{\Delta} PbO_2(s) + 2NO_2(g)$

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 23.3.1

Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $NO(g) + H_2O(l) \xrightarrow{\Delta}$
b. $NH_4NO_3(s) \xrightarrow{\Delta}$
c. $Sr(s) + N_2(g) \rightarrow$

Answer

a. $NO(g) + H_2O(l) \xrightarrow{\Delta}$ no reaction
b. $NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(g)$
c. $3Sr(s) + N_2(g) \rightarrow Sr_3N_2(s)$

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:

$$\mathrm{AsF_5(soln) + F^-(soln) \rightarrow AsF_6^-(soln)} \tag{22.5.4}$$

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, $\mathrm{H_3PO_3}$ and $\mathrm{H_3AsO_3}$, where E is P or As:

$$\mathrm{EX_3\,(l) + 3\,H_2O\,(l) \rightarrow H_3EO_3\,(aq) + 3\,HX\,(aq)} \tag{22.5.5}$$

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 22.5.2), 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 22.5.2. In contrast, Bi_2O_5 is so unstable that there is no absolute proof it exists.

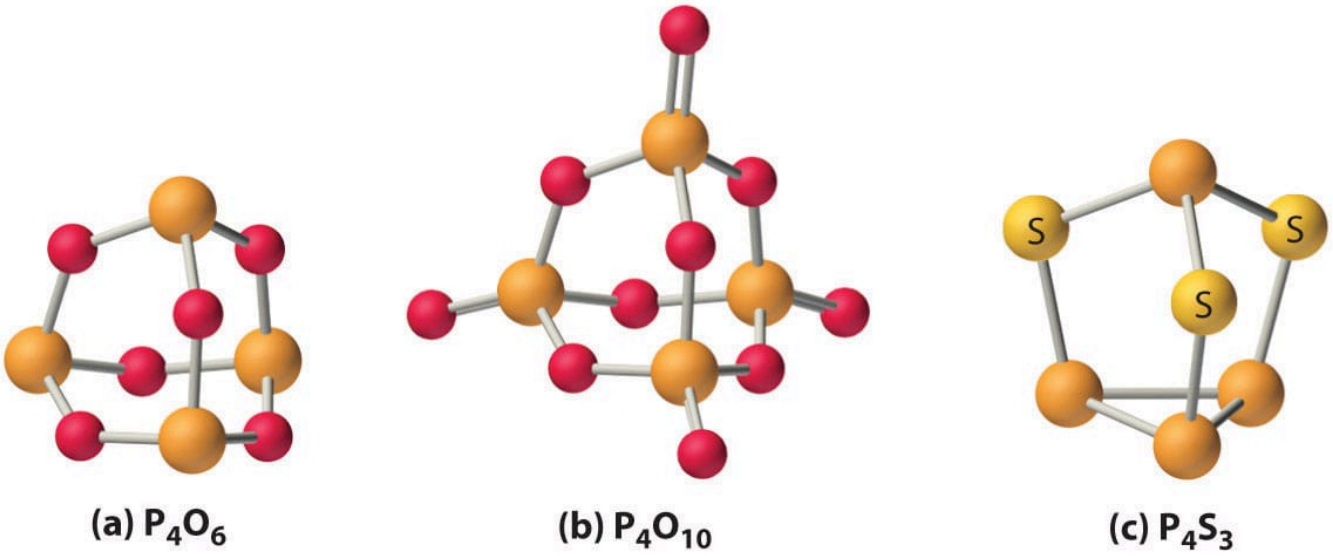


Figure 22.5.2: The Structures of Some Cage Compounds of Phosphorus. (a, b) The structures of P_4O_6 and P_4O_{10} are both derived from the structure of white phosphorus (P_4) by inserting an oxygen atom into each of the six edges of the P_4 tetrahedron; P_4O_{10} contains an additional terminal oxygen 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 22.5.2), 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 22.5.2

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 22.5.2

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. Nitrogen forms compounds in nine different oxidation states. 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. 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. 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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22.6: Hydrogen: A Unique Element

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 22.6.1 "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 22.6.1: 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	~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 22.6.1):

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.

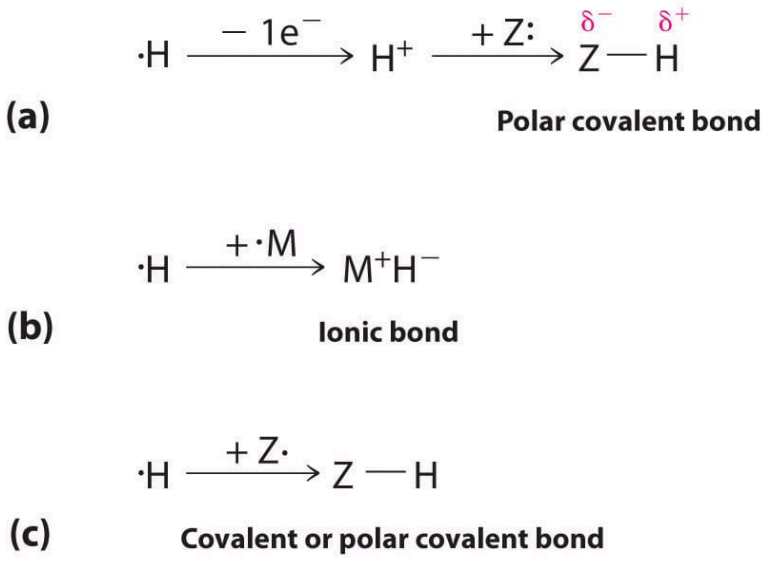


Figure 22.6.1: Three Types of Bonding in Compounds of Hydrogen. Because of its $1s^1$ electron configuration and the fact that the 1s orbital can accommodate no more than two electrons, hydrogen can (a) bond to other elements by losing an electron to form a proton, which can accept a pair of electrons 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 22.6.2). An example of this kind of interaction is the hydrogen bonding network found in water (Figure 22.6.2). 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.

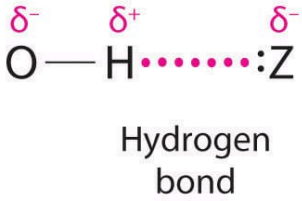


Figure 22.6.2: The Hydrogen Bond. The covalent bond between hydrogen and a very electronegative element, such as nitrogen, oxygen, or fluorine, is highly polar. The resulting partial positive charge on H allows it to interact with a lone pair of electrons on another atom to form a hydrogen bond, which 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 22.6.3). 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.

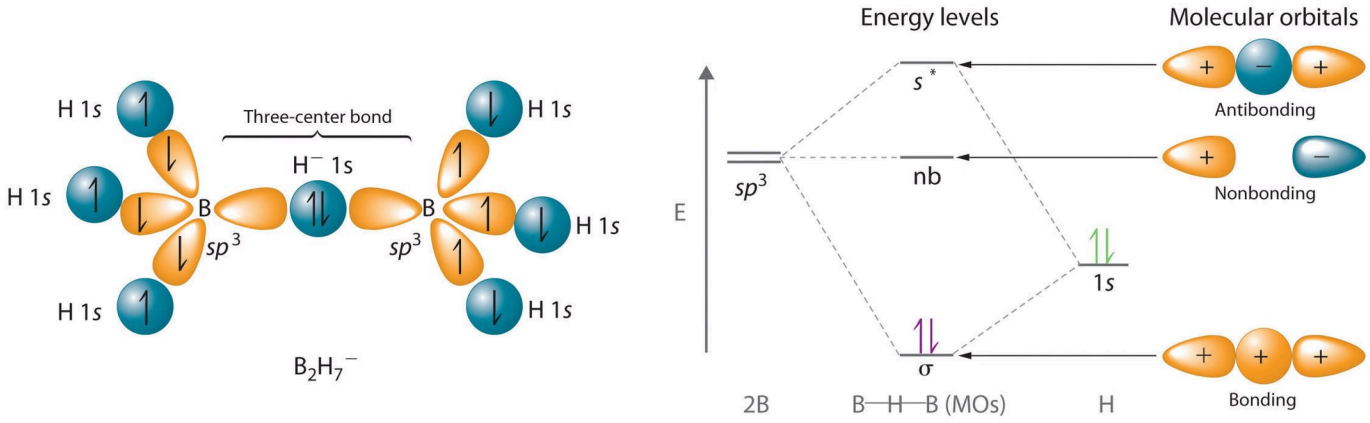


Figure 22.6.3: A Three-Center Bond Uses Two Electrons to Link Three Atoms. In the B–H–B unit shown, a hydride, with a filled 1s orbital, interacts simultaneously with empty sp^3 hybrids on the boron atoms of two BH_3 units to give three molecular orbitals. The two bonding electrons occupy the lowest-energy (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 22.6.4). 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).

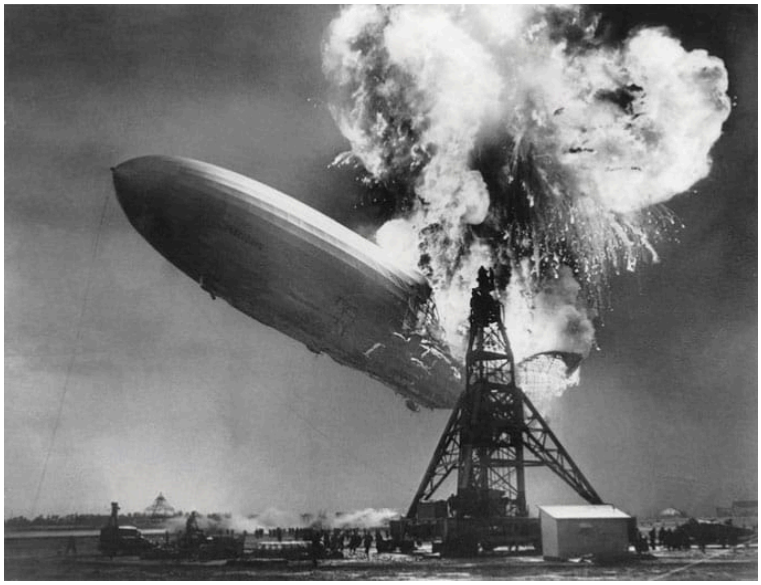


Figure 22.6.4: The Explosive Properties of Hydrogen. When mixed with air and ignited by a spark, hydrogen gas can explode. The photograph shows the German dirigible Hindenburg on fire at Lakehurst, New Jersey, in 1937, after its hydrogen compartment was accidentally ignited as a consequence of an electrical 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:

$$M_{(s)} + 2H^+_{(aq)} \rightarrow H_{2(g)} + M^{2+}_{(aq)} \tag{22.6.1}$$

Hydrogen gas can also be generated by reacting metals such as aluminum or zinc with a strong base:

$$\mathrm{Al(s) + OH^-(aq) + 3H_2O(l) \rightarrow \frac{3}{2}H_2(g) + [Al(OH)_4]^-(aq)} \tag{22.6.2}$$

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:

$$MH_{(s)} + D_2O(l) \rightarrow HD_{(g)} + M^+(aq) + OD^-_{(aq)} \tag{22.6.3}$$

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:

$$\mathrm{CH_4(g) + H_2O(g) \xrightarrow{Ni} CO(g) + 3H_2(g)} \tag{22.6.4}$$

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.E: Exercises

22.1: Periodic Trends in Bonding

Problems

1. Can an oxide be neither acidic nor basic?
2. $Rb + O_2\ (excess) \rightarrow\ ?$
3. $Na + O_2 \rightarrow\ ?$
4. BaO_2 is which of the following: hydroxide, peroxide, or superoxide?
5. What is an amphoteric solution?
6. Why is it difficult to obtain oxygen directly from water?

Solutions

1. Yes, an example is carbon monoxide (CO). CO doesn't produce a salt when reacted with an acid or a base.
2. $Rb + O_2\ (excess) \rightarrow RbO_2$
   With the presence of excess oxygen, Rubidium forms a superoxide. Please review section regarding basic oxides above for more detail.
3. $2Na + O_2 \rightarrow Na_2O$
   Note: The problem does not specify that the oxygen was in excess, so it cannot be a peroxide. Please review section regarding basic oxides for more detail.
4. BaO_2 is a peroxide. Barium has an oxidation state of +2 so the oxygen atoms have oxidation state of -1. As a result, the compound is a peroxide, but more specifically referred to as barium peroxide.
5. An amphoteric solution is a substance that can chemically react as either acid or base. See section above on Properties of Amphoteric Oxides for more detail.
6. Water as such is a neutral stable molecule. It is difficult to break the covalent O-H bonds easily. Hence, electrical energy through the electrolysis process is applied to separate dioxygen from water. When a small amount of acid is added to water ionization is initiated which helps in electrochemical reactions as follows.

$$[H_2O\ (acidulated) \rightleftharpoons H^+\ (aq) + OH]^- \times 4 \tag{22.E.1}$$

At cathode:

$$[H^+\ (aq) + e^- \rightarrow \frac{1}{2} H_2(g)] \times 4 \tag{22.E.2}$$

At anode:

$$4OH^-\ (aq) \rightarrow O_2 + 2H_2O + 4e^- \tag{22.E.3}$$

Net reaction:

$$2H_2O \xrightarrow{electrolysis} 2H_2\ (g) + O_2\ (g) \tag{22.E.4}$$

Oxygen can thus be obtained from acidified water by its electrolysis.

22.2: Group 18: The Noble Gases

Conceptual Problems

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. $Bi(s) + \text{excess } Br_2(l)$

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)] $\rightarrow 2DF(g) + CaSO_4(s)$

22.3: Group 17: The Halogens

Conceptual Problems

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. $8S^{2-}(aq) + 8I_2(aq) \rightarrow S_8(s) + 16I^-(aq)$

22.4: Group 16: The Oxygen Family

Conceptual Problems

1. Unlike the other chalcogens, oxygen does not form compounds in the +4 or +6 oxidation state. Why?
2. Classify each oxide as basic, acidic, amphoteric, or neutral.
   a. CaO

b. SO_2
c. NO
d. Rb_2O
e. PbO_2

3. Classify each oxide as basic, acidic, amphoteric, or neutral.
   a. BaO
   b. Br_2O
   c. SnO
   d. B_2O_3
   e. Sb_2O_3

4. Polarization of an oxide affects its solubility in acids or bases. Based on this, do you expect RuO_2 to be an acidic, a basic, or a neutral oxide? Is the compound covalent? Justify your answers.
5. Arrange CrO_3, Al_2O_3, Sc_2O_3, and BaO in order of increasing basicity.
6. As the atomic number of the group 16 elements increases, the complexity of their allotropes decreases. What factors account for this trend? Which chalcogen do you expect to polymerize the most readily? Why?
7. Arrange H_3BO_3, HIO_4, and HNO_2 in order of increasing acid strength.
8. Of OF_2, SO_2, P_4O_6, SiO_2, and Al_2O_3, which is most ionic?
9. Of CO_2, NO_2, O_2, SO_2, Cl_2O, H_2O, NH_3, and CH_4, which do you expect to have the

   a. most polar covalent bond(s)?
   b. least polar covalent bond(s)?

10. Of Na_2O_2, MgO, Al_2O_3, and SiO_2, which is most acidic?

11. Give an example of
    a. a covalent hydride that engages in strong hydrogen bonding.
    b. an amphoteric oxide.

12. The Si–O bond is shorter and stronger than expected. What orbitals are used in this bond? Do you expect Si to interact with Br in the same way? Why or why not?

Answers

1. Oxygen has the second highest electronegativity of any element; consequently, it prefers to share or accept electrons from other elements. Only with fluorine does oxygen form compounds in positive oxidation states.
3.

   a. basic
   b. acidic
   c. amphoteric
   d. acidic
   e. amphoteric

5. $CrO_3 < Al_2O_3 < Sc_2O_3 < BaO$

7. $H_3BO_3 < HNO_2 < HIO_4$

9. Most polar: H_2O; least polar: O_2
11.

    a. H_2O, HF, or NH_3
    b. SnO or Al_2O_3

Structure and Reactivity

1. Considering its position in the periodic table, predict the following properties of selenium:
   a. chemical formulas of its most common oxide, most common chloride, and most common hydride
   b. solubility of its hydride in water, and the acidity or basicity of the resulting solution
   c. the principal ion formed in aqueous solution

2. Using arguments based on electronegativity, explain why ZnO is amphoteric. What product would you expect when ZnO reacts with an aqueous
   a. acid?
   b. base?

3. Write a balanced chemical equation for the reaction of sulfur with
   a. $O_2(g)$.
   b. $S^{2-}(aq)$.
   c. $F_2(g)$.
   d. $HNO_3(aq)$.

Answer

3. a. $S_8 + 8O_2 \xrightarrow{\Delta} 8SO_2(g)$
   b. $S_8(s) + 8S^{2-}(aq) \rightarrow 8{S_2}^{2-}(aq)$
   c. $S_8(s) + 24F_2(g) \rightarrow 8SF_6(g)$
   d. $S_8(s) + 48HNO_3(aq) \rightarrow 8H_2SO_4(aq) + 48NO_2(g) + 16H_2O(l)$

22.5: Group 15: The Nitrogen Family

Conceptual Problems

1. Nitrogen is the first diatomic molecule in the second period of elements. Why is N_2 the most stable form of nitrogen? Draw its Lewis electron structure. What hybrid orbitals are used to describe the bonding in this molecule? Is the molecule polar?
2. The polymer $(SN)_n$ has metallic luster and conductivity. Are the constituent elements in this polymer metals or nonmetals? Why does the polymer have metallic properties?
3. Except for NF_3, all the halides of nitrogen are unstable. Explain why NF_3 is stable.
4. Which of the group 15 elements forms the most stable compounds in the +3 oxidation state? Explain why.
5. Phosphorus and arsenic react with the alkali metals to produce salts with the composition M_3Z_{11}. Compare these products with those produced by reaction of P and As with the alkaline earth metals. What conclusions can you draw about the types of structures favored by the heavier elements in this part of the periodic table?

Structure and Reactivity

1. PF_3 reacts with F_2 to produce PF_5, which in turn reacts with F^- to give salts that contain the ${PF_6}^-$ ion. In contrast, NF_3 does not react with F_2, even under extreme conditions; NF_5 and the ${NF_6}^-$ ion do not exist. Why?
2. Red phosphorus is safer to handle than white phosphorus, reflecting their dissimilar properties. Given their structures, how do you expect them to compare with regard to reactivity, solubility, density, and melting point?
3. Bismuth oxalate $[Bi_2(C_2O_4)_3]$ is a poison. Draw its structure and then predict its solubility in H_2O, dilute HCl, and dilute HNO_3. Predict its combustion products. Suggest a method to prepare bismuth oxalate from bismuth.
4. Small quantities of NO can be obtained in the laboratory by reaction of the iodide ion with acidic solutions of nitrite. Write a balanced chemical equation that represents this reaction.
5. Although pure nitrous acid is unstable, dilute solutions in water are prepared by adding nitrite salts to aqueous acid. Write a balanced chemical equation that represents this type of reaction.
6. Metallic versus nonmetallic behavior becomes apparent in reactions of the elements with an oxidizing acid, such as HNO_3. Write balanced chemical equations for the reaction of each element of group 15 with nitric acid. Based on the products,

predict which of these elements, if any, are metals and which, if any, are nonmetals.

7. Predict the product(s) of each reaction and then balance each chemical equation.

   a. $P_4O_{10}(s) + H_2O(l) \rightarrow$
   b. $AsCl_3(l) + H_2O(l) \rightarrow$
   c. $Bi_2O_3(s) + H_2O(l) \rightarrow$
   d. $Sb_4O_6(s) + OH^-(aq) \rightarrow$
   e. $(C_2H_5)_3Sb(l) + O_2(g) \xrightarrow{\Delta}$
   f. $SbCl_3(s) + LiAlH_4(soln) \rightarrow$
   g. $Ca(s) + N_2O(g) \xrightarrow{\Delta}$

8. Write a balanced chemical equation to show how you would prepare each compound.
   a. H_3PO_4 from P
   b. Sb_2O_5 from Sb
   c. SbH_3 from Sb

Answers

5. $NaNO_2(s) + HCl(aq) \rightarrow HNO_2(aq) + NaCl(aq)$
7.

   a. $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$
   b. $AsCl_3(l) + 3H_2O(l) \rightarrow H_3AsO_3(aq) + 3HCl(aq)$
   c. $Bi_2O_3(s) + 3H_2O(l) \rightarrow 2Bi(OH)_3(s)$
   d. $Sb_4O_6(s) + 4OH^-(aq) + 2H_2O(l) \rightarrow 4H_2SbO_3^-(aq)$
   e. $2(C_2H_5)3Sb(l) + 21O_2(g) \xrightarrow{\Delta} 12CO_2(g) + 15H_2O(g) + Sb_2O_3(s)$
   f. $4SbCl_3(s) + 3LiAlH_4(soln) \rightarrow 4SbH_3(g) + 3LiCl(soln) + 3AlCl_3(soln)$
   g. $Ca(s) + N_2O(g) \xrightarrow{\Delta} CaO(s) + N_2(g)$

22.6: Hydrogen: A Unique Element

Problems

1. Some periodic tables include hydrogen as a group 1 element, whereas other periodic tables include it as a group 17 element. Refer to the properties of hydrogen to propose an explanation for its placement in each group. In each case, give one property of hydrogen that would exclude it from groups 1 and 17.
2. If there were a planet where the abundances of D_2O and H_2O were reversed and life had evolved to adjust to this difference, what would be the effects of consuming large amounts of H_2O?
3. Describe the bonding in a hydrogen bond and the central B–H bond in $B_2H_7^-$. Why are compounds containing isolated protons unknown?
4. With which elements does hydrogen form ionic hydrides? covalent hydrides? metallic hydrides? Which of these types of hydrides can behave like acids?
5. Indicate which elements are likely to form ionic, covalent, or metallic hydrides and explain your reasoning:

   a. Sr
   b. Si
   c. O
   d. Li
   e. B
   f. Be
   g. Pd
   h. Al

6. Which has the higher ionization energy—H or H^-? Why?

7. The electronegativities of hydrogen, fluorine, and iodine are 2.20, 3.98, and 2.66, respectively. Why, then, is HI a stronger acid than HF?

8. If H_2O were a linear molecule, would the density of ice be less than or greater than that of liquid water? Explain your answer.

9. In addition to ion–dipole attractions, hydrogen bonding is important in solid crystalline hydrates, such as $Na_4XeO_6 \cdot 8H_2O$. Based on this statement, explain why anhydrous Na_4XeO_6 does not exist.

Answers

1. H has one electron in an s orbital, like the group 1 metals, but it is also one electron short of a filled principal shell, like the group 17 elements. Unlike the alkali metals, hydrogen is not a metal. Unlike the halogens, elemental hydrogen is not a potent oxidant.

5. a. ionic; it is an alkaline earth metal.
   b. covalent; it is a semimetal.
   c. covalent; it is a nonmetal.
   d. ionic; it is an alkali metal.
   e. covalent; it is a semimetal.
   f. covalent; it is a period 2 alkaline earth metal.
   g. metallic; it is a transition metal.
   h. covalent; it is a group 13 metal.

9. Hydrogen bonding with waters of hydration will partially neutralize the negative charge on the terminal oxygen atoms on the XeO_6^{4-} ion, which stabilizes the solid.

Structure and Reactivity

1. One of the largest uses of methane is to produce syngas, which is a source of hydrogen for converting nitrogen to ammonia. Write a complete equation for formation of syngas from methane and carbon dioxide. Calculate $\Delta G°$ for this reaction at 298 K and determine the temperature at which the reaction becomes spontaneous.

2. An alternative method of producing hydrogen is the water–gas shift reaction:

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

   Calculate $\Delta G°$ for this reaction at 298 K and determine the temperature at which the reaction changes from spontaneous to nonspontaneous (or vice versa).

3. Predict the products of each reaction at 25°C and then balance each chemical equation.
   a. $CsH(s) + D_2O(l) \rightarrow$
   b. $CH_3CO_2H(l) + D_2O(l) \rightarrow$
   c. $H_3PO_4(aq) + D_2O(l) \rightarrow$
   d. $NH_2CH_2CO_2H(s) + D_2O(l) \rightarrow$
   e. $NH_4Cl(s) + D_2O(l) \rightarrow$

4. Using heavy water (D_2O) as the source of deuterium, how could you conveniently prepare
   a. D_2SO_4?
   b. LiD?

5. What are the products of reacting NaH with D_2O? Do you expect the same products from reacting NaD and H_2O? Explain your answer.

6. A 2.50 g sample of zinc metal reacts with 100.0 mL of 0.150 M HCl. What volume of H_2 (in liters) is produced at 23°C and 729 mmHg?

7. A chemical reaction requires 16.8 L of H_2gas at standard temperature and pressure. How many grams of magnesium metal are needed to produce this amount of hydrogen gas?

8. Seawater contains 3.5% dissolved salts by mass and has an average density of 1.026 g/mL. The volume of the ocean is estimated to be 1.35×10^{21} L. Using the data in Table $22.E.1$, calculate the total mass of deuterium in the ocean.

9. From the data in Table $22.E.1$, determine the molarity of DOH in water. Do you expect the molarity of D_2O in water to be similar? Why or why not?

10. From the data in Table $22.E.1$, calculate how many liters of water you would have to evaporate to obtain 1.0 mL of TOD (tritium-oxygen-deuterium). The density of TOD is 1.159 g/mL.

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23: THE TRANSITION ELEMENTS

Petrucci: *General Chemistry*
Principles and Modern Applications

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23.1: General Properties of Transition Metals

We have daily contact with many transition metals. Iron occurs everywhere—from the rings in your spiral notebook and the cutlery in your kitchen to automobiles, ships, buildings, and in the hemoglobin in your blood. Titanium is useful in the manufacture of lightweight, durable products such as bicycle frames, artificial hips, and jewelry. Chromium is useful as a protective plating on plumbing fixtures and automotive detailing.

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. As shown in Figure 23.1.2, the *d*-block elements in groups 3–11 are transition elements. The *f*-block elements, also called *inner transition metals* (the lanthanides and actinides), also meet this criterion because the *d* orbital is partially occupied before the *f* orbitals. The *d* orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.



Figure 23.1.1: Transition metals often form vibrantly colored complexes. The minerals malachite (green), azurite (blue), and proustite (red) are some examples. (credit left: modification of work by James St. John; credit middle: modification of work by Stephanie Clifford; credit right: modification of work by Terry Wallace)

The *d*-block elements are divided into the first transition series (the elements Sc through Cu), the second transition series (the elements Y through Ag), and the third transition series (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the fourth transition series, which also includes Rf through Rg.

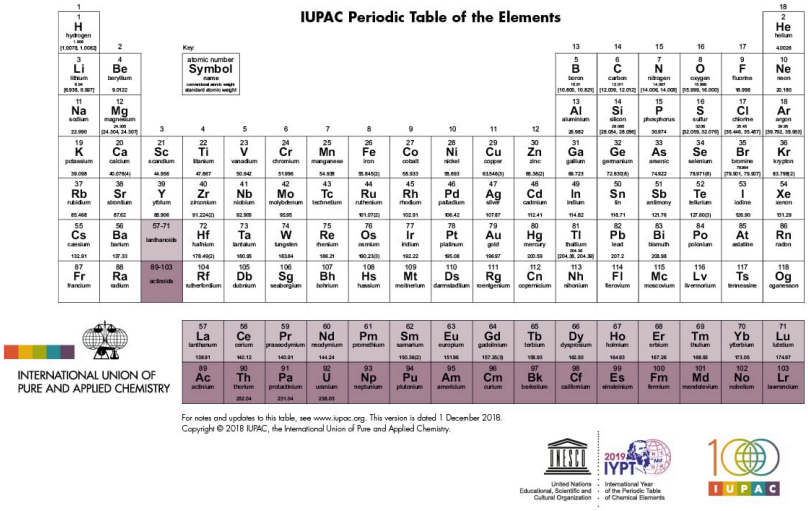


Figure 23.1.2: The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

The *f*-block elements are the elements Ce through Lu, which constitute the lanthanide series (or lanthanoid series), and the elements Th through Lr, which constitute the actinide series (or actinoid series). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series

Properties and Trends in Transition Metals

The elements of the second and third rows of the Periodic Table show gradual changes in properties across the table from left to right as expected. Electrons in the outer shells of the atoms of these elements have little shielding effects resulting in an increase in effective nuclear charge due to the addition of protons in the nucleus. Consequently, the effects on atomic properties are: smaller atomic radius, increased first ionization energy, enhanced electronegativity and more nonmetallic character. This trend continues until one reaches calcium (Z=20). There is an abrupt break at this point. The next ten elements called the first transition series are remarkably similar in their physical and chemical properties. This general similarity in properties has been explained in terms of their relatively small difference in effective nuclear charge over the series. This occurs because each additional electron enters the penultimate 3d shell providing an effective shield between the nucleus and the outer 4s shell.

What is a Transition Metal?

Thus, the transition elements can be defined as those in which the d electron shells are being filled and so we generally ignore Sc and Zn where Sc(III) is d^0 and Zn(II) is d^{10}.

It is useful, at the beginning, to identify the physical and chemical properties of transition elements which differ from main group elements (s-block). Properties of transition elements include:

- have large charge/radius ratio;
- are hard and have high densities;
- have high melting and boiling points;
- form compounds which are often paramagnetic;
- show variable oxidation states;
- form coloured ions and compounds;
- form compounds with profound catalytic activity;
- form stable complexes.

Table 23.1.1 : Summary of select physical properties of transition elements:

Element	Group	density /g cm^{-3}	m. p. / °C	b.p. / °C	radius / pm	free atom configuration	ionization energy / kJ mol^{-1}	Uses
Sc	3	2.99	1541	2831	164	[Ar] $3d^1 4s^2$	631	
Ti	4	4.50	1660	3287	147	[Ar]$3d^2 4s^2$	658	-engines/aircraft industry-density is 60% of iron
V	5	5.96	1890	3380	135	[Ar]$3d^3 4s^2$	650	-stainless steel, 19% Cr, 9% Ni the rest Fe
Cr	6	7.20	1857	2670	129	[Ar]$3d^5 4s^1$	653	-alloys eg with C steel, the most significant use
Mn	7	7.20	1244	1962	137	[Ar]$3d^5 4s^2$	717	-alloys eg with Cu
Fe	8	7.86	1535	2750	126	[Ar]$3d^6 4s^2$	759	-alloys eg with C steel, the most significant use
Co	9	8.90	1495	2870	125	[Ar]$3d^7 4s^2$	758	-alloys eg with Cr and W for hardened drill bits

Element	Group	density /g cm^{-3}	m. p. / °C	b.p. / °C	radius / pm	free atom configuration	ionization energy / kJ mol^{-1}	Uses
Ni	10	8.90	1455	2730	125	$[Ar]3d^8 4s^2$	737	-alloys Fe/Ni armor plating, resists corrosion
Cu	11	8.92	1083	2567	128	$[Ar]3d^{10} 4s^1$	746	-high electrical conductivity (2nd to Ag), wiring
Zn	12	7.14	420	907	137	$[Ar]3d^{10} 4s^2$	906	

Densities and Metallic Radii

The transition elements are much denser than the s-block elements and show a gradual increase in density from scandium to copper. This trend in density can be explained by the small and irregular decrease in metallic radii coupled with the relative increase in atomic mass.

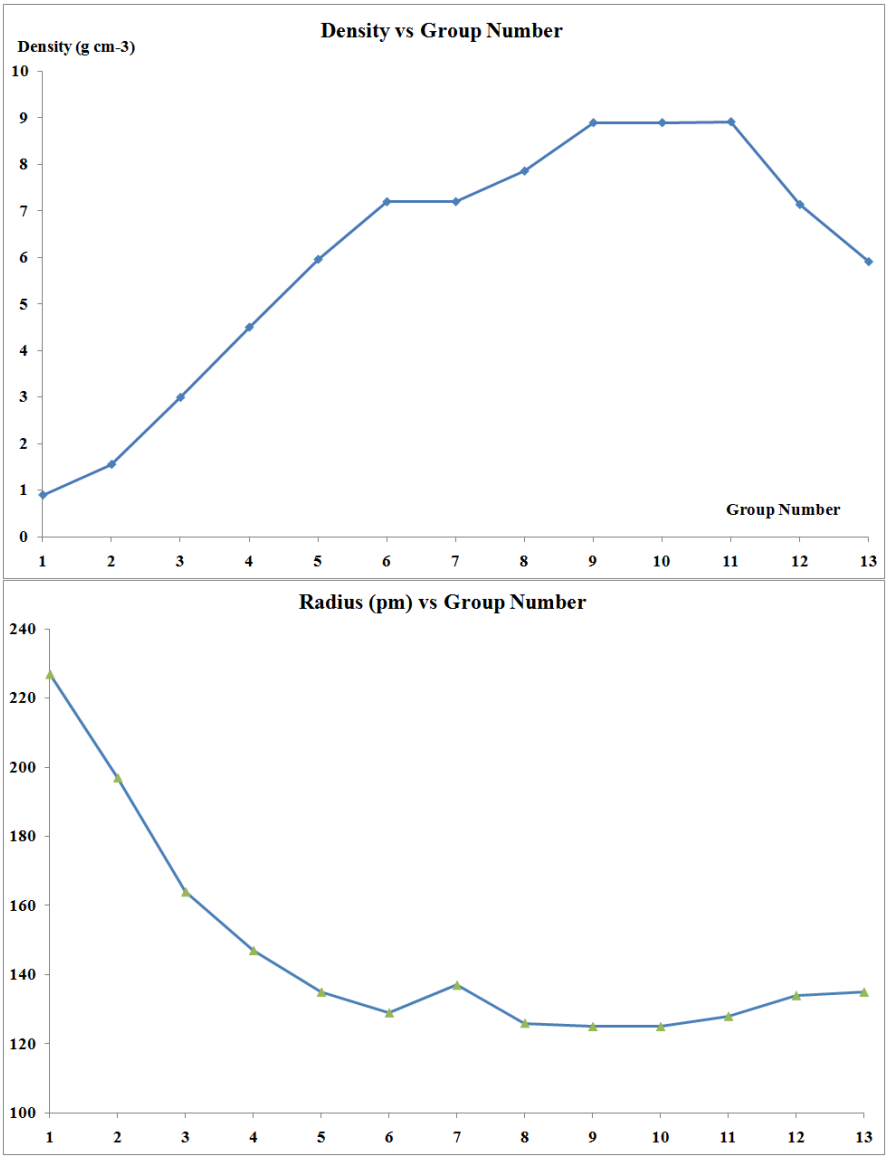


Figure 23.1.3: Variations of the density (leff) and metallic radius (right) in the first row transition metals.

Melting and Boiling points

The melting points and the molar enthalpies of fusion of the transition metals are both high in comparison to main group elements. This arises from strong metallic bonding in transition metals which occurs due to delocalization of electrons facilitated by the availability of both d and s electrons.

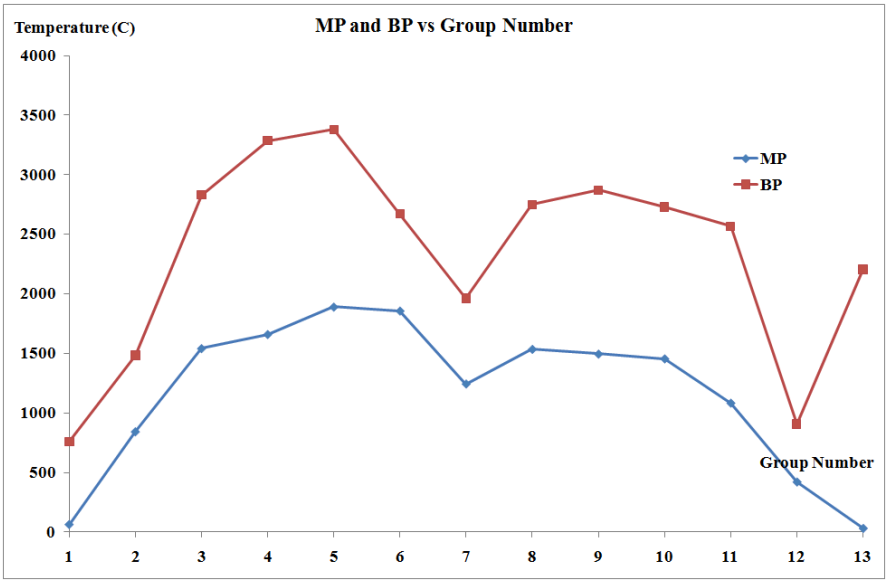


Figure 23.1.4: Variations of the melting point (blue curve) and boiling points (red) in the first row transition metals.

Ionization Energies

In moving across the series of metals from scandium to zinc a small change in the values of the first and second ionization energies is observed. This is due to the build-up of electrons in the immediately underlying d-sub-shells that efficiently shields the 4s electrons from the nucleus and minimizing the increase in effective nuclear charge Z_{eff} from element to element. The increases in third and fourth ionization energy values are more rapid. However, the trends in these values show the usual discontinuity half way along the series. The reason is that the five d electrons are all unpaired, in singly occupied orbitals. When the sixth and subsequent electrons enter, the electrons have to share the already occupied orbitals resulting in inter-electron repulsions, which would require less energy to remove an electron. Hence, the third ionization energy curve for the last five elements is identical in shape to the curve for the first five elements, but displaced upwards by 580 kJ mol^{-1}.

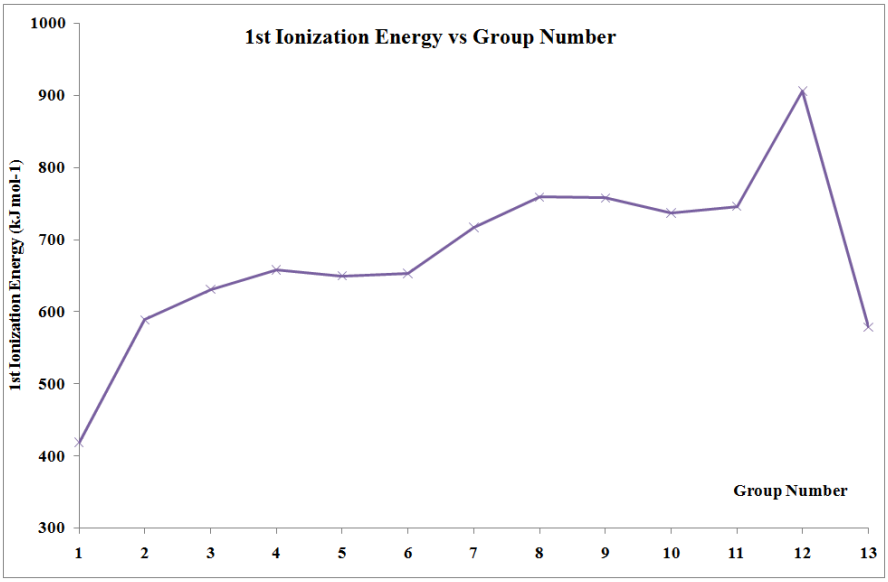


Figure 23.1.4: Variations of the first ionization energy in the first row transition metals.

Oxidation States

Transition metals can form compounds with a wide range of oxidation states. Some of the observed oxidation states of the elements of the first transition series are shown in Figure 23.1.5. As we move from left to right across the first transition series, we see that the number of common oxidation states increases at first to a maximum towards the middle of the table, then decreases. The values in the table are typical values; there are other known values, and it is possible to synthesize new additions. For example, in 2014, researchers were successful in synthesizing a new oxidation state of iridium (9+).

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
								1+	
		2+	2+	2+	2+	2+	2+	2+	2+
3+	3+	3+	3+	3+	3+	3+	3+	3+	
	4+	4+	4+	4+					
		5+							
			6+	6+	6+				
				7+					

Figure 23.1.5:Transition metals of the first transition series can form compounds with varying oxidation states.

For the elements scandium through manganese (the first half of the first transition series), the highest oxidation state corresponds to the loss of all of the electrons in both the *s* and *d* orbitals of their valence shells. The titanium(IV) ion, for example, is formed when the titanium atom loses its two 3*d* and two 4*s* electrons. These highest oxidation states are the most stable forms of scandium, titanium, and vanadium. However, it is not possible to continue to remove all of the valence electrons from metals as we continue through the series. Iron is known to form oxidation states from 2+ to 6+, with iron(II) and iron(III) being the most common. Most of the elements of the first transition series form ions with a charge of 2+ or 3+ that are stable in water, although those of the early members of the series can be readily oxidized by air.

The elements of the second and third transition series generally are more stable in higher oxidation states than are the elements of the first series. In general, the atomic radius increases down a group, which leads to the ions of the second and third series being larger than are those in the first series. Removing electrons from orbitals that are located farther from the nucleus is easier than removing electrons close to the nucleus. For example, molybdenum and tungsten, members of group 6, are limited mostly to an oxidation state of 6+ in aqueous solution. Chromium, the lightest member of the group, forms stable Cr^{3+} ions in water and, in the absence of air, less stable Cr^{2+} ions. The sulfide with the highest oxidation state for chromium is Cr_2S_3, which contains the Cr^{3+} ion. Molybdenum and tungsten form sulfides in which the metals exhibit oxidation states of 4+ and 6+.

Electronic Configurations

The electronic configuration of the atoms of the first row transition elements are basically the same. It can be seen in the Table above that there is a gradual filling of the 3d orbitals across the series starting from scandium. This filling is, however, not regular, since at chromium and copper the population of 3d orbitals increase by the acquisition of an electron from the 4s shell. This illustrates an important generalization about orbital energies of the first row transition series. At chromium, both the 3d and 4s orbitals are occupied, but neither is completely filled in preference to the other. This suggests that the energies of the 3d and 4s orbitals are relatively close for atoms in this row.

In the case of copper, the 3d level is full, but only one electron occupies the 4s orbital. This suggests that in copper the 3d orbital energy is lower than the 4s orbital. Thus the 3d orbital energy has passed from higher to lower as we move across the period from potassium to zinc. However, the whole question of preference of an atom to adopt a particular electronic configuration is not determined by orbital energy alone. In chromium it can be shown that the 4s orbital energy is still below the 3d which suggests a configuration [Ar] $3d^4 4s^2$. However due to the effect of electronic repulsion between the outer electrons the actual configuration becomes [Ar]$3d^5 4s^1$ where all the electrons in the outer orbitals are unpaired. It should be remembered that the factors that determine electronic configuration in this period are indeed delicately balanced.

Redox Couple	E°/V
$Mn^{2+}(aq.)/Mn(s)$	-1.18
$H^+(aq.)/H_2(g)$	0.00

This shows that elemental Mn is a stronger reductant than molecular hydrogen and hence should be able to displace hydrogen gas from 1 mol dm^{-3} hydrochloric acid.

Valence Electrons in Transition Metals

Review how to write electron configurations, covered in the chapter on electronic structure and periodic properties of elements. Recall that for the transition and inner transition metals, it is necessary to remove the *s* electrons before the *d* or *f* electrons. Then, for each ion, give the electron configuration:

a. cerium(III)
b. lead(II)
c. Ti^{2+}
d. Am^{3+}
e. Pd^{2+}

For the examples that are transition metals, determine to which series they belong.

Solution

For ions, the *s*-valence electrons are lost prior to the *d* or *f* electrons.

a. Ce^{3+}[Xe]$4f^1$; Ce^{3+} is an inner transition element in the lanthanide series.
b. Pb^{2+}[Xe]$6s^2 5d^{10} 4f^{14}$; the electrons are lost from the *p* orbital. This is a main group element.
c. titanium(II) [Ar]$3d^2$; first transition series
d. americium(III) [Rn]$5f^6$; actinide
e. palladium(II) [Kr]$4d^8$; second transition series

Exercise 23.1.1

Check Your Learning Give an example of an ion from the first transition series with no *d* electrons.

Answer

V^{5+} is one possibility. Other examples include Sc^{3+}, Ti^{4+}, Cr^{6+}, and Mn^{7+}.

Chemical Reactivity

Transition metals demonstrate a wide range of chemical behaviors. As can be seen from their reduction potentials (Table P1), some transition metals are strong reducing agents, whereas others have very low reactivity. For example, the lanthanides all form stable 3+ aqueous cations. The driving force for such oxidations is similar to that of alkaline earth metals such as Be or Mg, forming Be^{2+} and Mg^{2+}. On the other hand, materials like platinum and gold have much higher reduction potentials. Their ability to resist oxidation makes them useful materials for constructing circuits and jewelry.

Ions of the lighter *d*-block elements, such as Cr^{3+}, Fe^{3+}, and Co^{2+}, form colorful hydrated ions that are stable in water. However, ions in the period just below these (Mo^{3+}, Ru^{3+}, and Ir^{2+}) are unstable and react readily with oxygen from the air. The majority of simple, water-stable ions formed by the heavier *d*-block elements are oxyanions such as $\mathrm{MoO_4{}^{2-}}$ and $\mathrm{ReO_4{}^-}$.

Ruthenium, osmium, rhodium, iridium, palladium, and platinum are the "*platinum metals*". With difficulty, they form simple cations that are stable in water, and, unlike the earlier elements in the second and third transition series, they do not form stable oxyanions.

Both the *d*- and *f*-block elements react with nonmetals to form binary compounds; heating is often required. These elements react with halogens to form a variety of halides ranging in oxidation state from 1+ to 6+. On heating, oxygen reacts with all of the transition elements except palladium, platinum, silver, and gold. The oxides of these latter metals can be formed using other reactants, but they decompose upon heating. The *f*-block elements, the elements of group 3, and the elements of the first transition series except copper react with aqueous solutions of acids, forming hydrogen gas and solutions of the corresponding salts.

Activity of the Transition Metals

Which is the strongest oxidizing agent in acidic solution: dichromate ion, which contains chromium(VI), permanganate ion, which contains manganese(VII), or titanium dioxide, which contains titanium(IV)?

Solution

First, we need to look up the reduction half reactions (Table P1) for each oxide in the specified oxidation state:

$$\mathrm{Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \quad +1.33\ V} \tag{23.1.1}$$

$$\mathrm{MnO_4{}^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + H_2O \quad +1.51\ V} \tag{23.1.2}$$

$$\mathrm{TiO_2 + 4\,H^+ + 2\,e^- \longrightarrow Ti^{2+} + 2\,H_2O \quad -0.50\ V} \tag{23.1.3}$$

A larger reduction potential means that it is easier to reduce the reactant. Permanganate, with the largest reduction potential, is the strongest oxidizer under these conditions. Dichromate is next, followed by titanium dioxide as the weakest oxidizing agent (the hardest to reduce) of this set.

Exercise 23.1.2

Predict what reaction (if any) will occur between HCl and Co(s), and between HBr and Pt(s). You will need to use the standard reduction potentials from (Table P1).

Answer

$\mathrm{Co}(s) + 2\,\mathrm{HCl} \longrightarrow \mathrm{H_2} + \mathrm{CoCl_2}(aq)$; no reaction because Pt(s) will not be oxidized by H^+

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23.2: Principles of Extractive Metallurgy

Learning Objectives

- Discuss how coordination chemistry can be applied in metallurgic processes.
- Understanding the thermodynamics of Pyrometallurgy

The Earth formed from the same cloud of matter that formed the Sun, but the planets acquired different compositions during the formation and evolution of the solar system. In turn, the natural history of the Earth caused parts of this planet to have differing concentrations of the elements. The mass of the Earth is approximately 5.98×1024 kg. In bulk, by mass, it is composed mostly of iron (32.1%), oxygen (30.1%), silicon (15.1%), magnesium (13.9%), sulfur (2.9%), nickel (1.8%), calcium (1.5%), and aluminum (1.4%); with the remaining 1.2% consisting of trace amounts of other elements. Figure 23.2.1 illustrates the relative atomic-abundance of the chemical elements in Earth's upper continental crust, which is relatively accessible for measurements and estimation.

Figure 23.2.1: *Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number. The rarest elements in the crust (shown in yellow) are not the heaviest, but are rather the siderophile (iron-loving) elements in the Goldschmidt classification of elements. These have been depleted by being relocated deeper into the Earth's core. Their abundance in meteoroids is higher. Additionally, tellurium and selenium have been depleted from the crust due to formation of volatile hydrides.*

Many of the elements shown in the graph are classified into (partially overlapping) categories:

1. rock-forming elements (major elements in green field, and minor elements in light green field);
2. rare earth elements (lanthanides, La-Lu, and Y; labeled in blue);
3. major industrial metals (global production >~3×10^7 kg/year; labeled in red);
4. precious metals (labeled in purple);
5. the nine rarest "metals" (the six platinum group elements and Au, Re, and Te) are in the yellow field.

Figure 23.2.2: Three Common Ores. (left) Iron ore, (middle) Manganese ore – psilomelane, and (right) Lead ore – galena and anglesite.

Most metals are found as types of rock in the Earth's crust. These ores contain sufficient minerals with important elements including metals that can be economically extracted from the rock. Metal ores are generally oxides, sulfides, silicates (Table 23.2.1) or "native" metals (such as native copper) that are not commonly concentrated in the Earth's crust, or "noble" metals (not usually forming compounds) such as gold (Figure 23.2.2). The ores must be processed to extract the metals of interest from the waste rock and from the ore minerals.

Figure 23.2.1: Composition of Earth's mantle in weight percent

Element	Amount	Compound	Amount
O	44.8		
Mg	22.8	SiO_2	46
Si	21.5	MgO	37.8
Fe	5.8	FeO	7.5
Ca	2.3	Al_2O_3	4.2
Al	2.2	CaO	3.2
Na	0.3	Na_2O	0.4
K	0.03	K_2O	0.04
Sum	99.7	Sum	99.1

Extractive metallurgy is a branch of metallurgical engineering wherein process and methods of extraction of metals from

their natural mineral deposits are studied. The field is a materials science, covering all aspects of the types of ore, washing, concentration, separation, chemical processes and extraction of pure metal and their alloying to suit various applications, sometimes for direct use as a finished product, but more often in a form that requires further working to achieve the given properties to suit the applications. The field of ferrous and non-ferrous extractive metallurgy have specialties that are generically grouped into the categories of mineral processing, hydrometallurgy, pyrometallurgy, and electrometallurgy based on the process adopted to extract the metal. Several processes are used for extraction of same metal depending on occurrence and chemical requirements.

It takes multiple steps to extract the "important" element from the ore:

1. First, the ore must be separated from unwanted rocks.
2. Then, the minerals need to be separated out of the ore
3. Since most minerals are not pure metals, further separation methods are required.

Most minerals are chemical compounds that contain metals and other elements.

Concentration

After mining, large pieces of the ore feed are broken through crushing and/or grinding. This step creates particles that are either mostly valuable or mostly waste. TConcentrating the particles of value in a form supporting separation enables the desired metal to be removed from waste products. Froth flotation is one process for separating minerals from the surrounding worthless material by taking advantage of differences in their *hydrophobicity*. whereby hydrophobicity differences between valuable minerals other material are increased through the use of surfactants and wetting agents (Figure 23.2.3). Flotation is used for the separation of a large range of sulfides, carbonates and oxides prior to further refinement. Phosphates and coal are also upgraded (purified) by flotation technology.



Figure 23.2.3: Diagram of a cylindrical froth flotation cell. The separation of the minerals makes processing complex (that is, mixed) ores economically feasible. Image used with permisison from Wikipedia (credit: Dhatfield).

Other ways to concentration minerals include approached based on density (Froth Flotation) used if ore density is less than density of impurities, or via melting points, or magnetic properties (Magnetic separation). This can be used with magnetic ores (i.e Fe_3O_4) that are passed through a magnetic field, which attracts the magnetic ore and ignore the nonmagnetic impurities.

Roasting

Ore is crushed and heated to a high temp using a strong blast of hot air. The process converts the ores to their oxides which can then be reduced. Consider the natural occurring ores of zinc (ZnS (sphalerite) and $ZnCO_3$ (smithsonite). When roasted, smithsonite decomposes to $ZnO_{(s)}$ and $CO_{2(g)}$ 23.2.1 and the hot air involved in roasting sphalerite oxidizes it 23.2.2 to produces

$ZnO_{(s)}$ and $SO_{2(g)}$.

$$ZnCO_{3(s)} \xrightarrow{\Delta} ZnO_{(s)} + CO_{2(g)} \tag{23.2.1}$$

$$2ZnS_{(s)} + 3O_{2(g)} \xrightarrow{\Delta} 2ZnO_{(s)} + 2SO_{2(g)} \tag{23.2.2}$$

Reduction

$C_{(s)}$ and $CO_{(g)}$ are often used as reducing agents in simultaneous reactions. Oxides of Cr, V, and Mn are reduced using Al. During the reduction process the metal oxide is heated to a temperature above its boiling point in order to vaporize it and condense as a liquid. For example, $ZnO_{(s)}$ that is produced in the roasting process is combined with $C_{(s)}/CO_{(g)}$ mixture and heated at a 1100 ^{o}C. Two reduction reactions are viable at this temperature with either carbon (Equation 23.2.3) or carbon monoxide ((Equation 23.2.4) acting the reducing agent.

$$ZnO_{(s)} + C_{(s)} \xrightarrow{\Delta} Zn_{(g)} + CO_{(g)} \tag{23.2.3}$$

$$ZnO_{(s)} + CO_{(g)} \xrightarrow{\Delta} Zn_{(g)} + CO_{2(g)} \tag{23.2.4}$$

Refining

The impurities contained in the metal product of the roasting/reduction process are removed. For example, the $Zn(l)$ produced in the reduction process often contains impurities of Cd and Pb. Though fractional distillation of Zn(l) will work in the refining process, a more commonly used and efficient method is electrolysis. The $ZnO_{(s)}$ produced from roasting is dissolved in $H_2SO_{4(aq)}$ and $Zn_{(s)}$ powder is added allowing the impurities to be displaced. The solution is then electrolyzed and to get a pure metallic $Zn_{(s)}$ as a result.

Zone Refining

A rod containing the desired pure metal and impurities is passed through a series of heating coils and cooled again. The process isolates the impurities that concentrate in the molten zones, leaving the portions behind them somewhat more pure. This process is repeated until impurities are moved to the end of the rod and cut off, resulting in an almost completely pure metal rod.

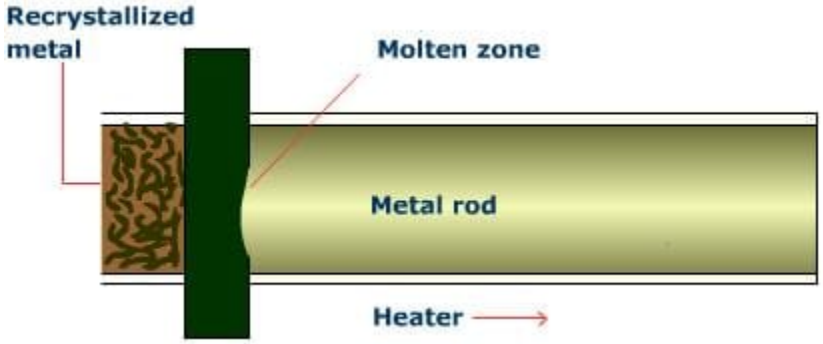


Figure 23.2.4: The Zone refining method. from Binod Shrestha.

Thermodynamics of Pyrometallurgy

Pyrometallurgy is the processes of roasting an ore a high temperatures and then reducing its oxide product. Its characteristics include:

1. large amount of waste as a product of concentration.
2. high energy consumption to maintain high temps.
3. gaseous emissions that must be controlled (i.e CO_2 and SO_2)

The oldest, and still the most common smelting process for oxide ores involves heating them in the presence of carbon. Originally, charcoal was used, but industrial-scale smelting uses coke, a crude form of carbon prepared by pyrolysis (heating) of coal. The basic reactions are:

$$MO + C \rightleftharpoons M + CO \tag{23.2.5}$$

$$MO + ½O_2 \rightleftharpoons M + ½CO_2 \tag{23.2.6}$$

$$MO + CO \rightleftharpoons M + CO_2 \tag{23.2.7}$$

Each of these can be regarded as a pair of *coupled reactions* in which the metal M and the carbon are effectively competing for the oxygen atom. Using reaction 23.2.5 as an example, it can be broken down into the following two parts:

$$MO \rightleftharpoons M + ½O_2 \quad \Delta G^o > 0 \tag{23.2.8}$$

$$C + ½O_2 \rightleftharpoons CO \quad \Delta G^o < 0 \tag{23.2.9}$$

At ordinary environmental temperatures, reaction 23.2.8 is always spontaneous in the reverse direction (that is why ores form in the first place!), so $\Delta G°$ of Reaction 23.2.8 will be positive. $\Delta G°$ for reaction 23.2.9 is always negative, but at low temperatures it will not be sufficiently negative to drive 23.2.8.

Figure 23.2.3 **:** *Coke is a fuel with few impurities and a high carbon content, usually made from coal. It is the solid carbonaceous material derived from destructive distillation of low-ash, low-sulfur bituminous coal. Cokes made from coal are grey, hard, and porous. While coke can be formed naturally, the commonly used form is man-made. Image used withpermission from Wikipedia (Stahlkocher).*

The *smelting* process depends on the different ways in which the free energies of reactions like 23.2.8 and 23.2.8 vary with the temperature. This temperature dependence is almost entirely dominated by the $T\Delta S°$ term in the Gibbs function, and thus by the entropy change. The latter depends mainly on Δn_g, the change in the number of moles of gas in the reaction. Removal of oxygen from the ore is always accompanied by a large increase in the system volume so ΔS for this step is always positive and the reaction becomes more spontaneous at higher temperatures. The temperature dependences of the reactions that take up oxygen vary, however (Table 23.2.1).

Table 23.2.2**:** *The temperature dependences of the reactions*

Reaction	**Δn_g**	**$d(\Delta G°)/dT$**
C + ½ O_2 → CO	0.5	<0
C + O_2 → CO_2	0	0
CO + ½ O_2 → CO_2	-0.5	>0

A plot of the temperature dependences of the free energies of these reactions, superimposed on similar plots for the oxygen removal reactions 23.2.8 is called an *Ellingham diagram*. For a given oxide MO to be smeltable, the temperature must be high enough that reaction 23.2.8 falls below that of at least one of the oxygen-consuming reactions. The slopes of the lines on this diagram are determined by the sign of the entropy change.

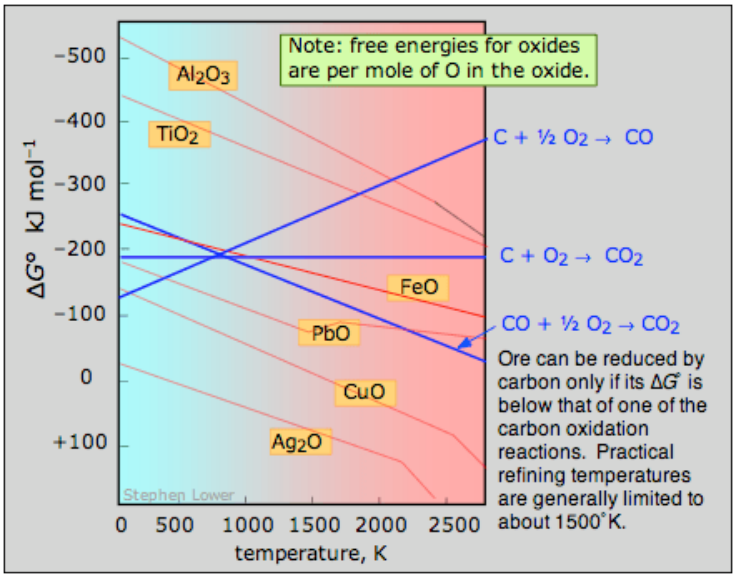


Figure 23.2.4***:*** *Ellingham diagram. An ore can be reduced by carbon only if its Gibbs free energy of formation falls below that of one of the carbon reduction reactions (blue lines.) Practical refining temperatures are generally limited to about 1500°K.*

Examination of the Ellingham diagram shown above illustrates why the metals known to the ancients were mainly those such as copper and lead, which can be obtained by smelting at the relatively low temperatures that were obtainable by the methods available at the time in which a charcoal fire supplied both the heat and the carbon. Thus the bronze age preceded the iron age; the latter had to await the development of technology capable of producing higher temperatures, such as the blast furnace. Smelting of aluminum oxide by carbon requires temperatures too high to be practical; commercial production of aluminum is accomplished by electrolysis of the molten ore.

In pyrometallurgy, an ore is heated with a reductant to obtain the metal. Theoretically, it should be possible to obtain virtually any metal from its ore by using coke as the reductant. For example, the reduction of calcum metral from $CaO_{(s)}$:

$$\mathrm{CaO(s) + C(s) \xrightarrow{\Delta} Ca(l) + CO(g)} \tag{23.2.10}$$

Unfortunately, many transition metals (e.g., Titanium) react with carbon to form stable binary carbides:

$$Ti + C \rightarrow TiC. \tag{23.2.11}$$

Consequently, more expensive reductants (such as hydrogen, aluminum, magnesium, or calcium) must be used to obtain these metals. Many metals that occur naturally as sulfides can be obtained by heating the sulfide in air, as shown for lead in the following equation:

$$\mathrm{PbS(s) + O_2(g) \xrightarrow{\Delta} Pb(l) + SO_2(g)} \tag{23.2.12}$$

The reaction is driven to completion by the formation of SO_2, a stable gas.

Iron Alloys of Cr, V, and Mn

1. *Ferrochrome* (alloy of Fe and Cr) can be produced in the reduction of Cr in an Fe compound containing its chromite ore, $Fe(CrO_2)_2$.
2. *Ferrovanadium* (alloy of Fe and V) can be produced in the reduction of V that occurs when adding an Fe compound to a V oxide (V_2O_5).
3. *Ferromanganese* (alloy of Fe and Mn) can be produced in the reduction of Mn that occurs when adding an Fe compound to a Mn oxide (MnO_2).

Titanium Production

Titanium is used in the military and aircraft industry b/c of its low density and ability to maintain its strength are high temps.



Figure 23.2.5: Titanium was used for 85% of the structure of Lockheed's's SR-71B Blackbird.

Titanium is produced using the following steps:

1. Conversion or rutile or TiO_2 to $TiCl_4$ with $C_{(s)}$ and Cl_2 under high heat (> 800 °C)

$$TiO_{2(s)} + 2C_{(s)} + 2Cl_{(2(g)} \xrightarrow{\Delta} Pb(l)TiCl_{4(g)} + 2CO_{(g)} \tag{23.2.13}$$

2. Reduction of $TiCl_4$ to Ti with a good reducing agent (i.e., Mg in the Kroll process) carried out at high heat (> 1000 °C).

$$TiCl_{4(g)} + 2Mg_{(l)} \xrightarrow{\Delta} Ti_{(s)} + 2MgCl_{2(s)} \tag{23.2.14}$$

3. Both $Ti_{(s)}$ and $MgCl_{2(s)}$ are electrolyzed to produces Cl_2, Mg and titanium sponge (Ti enriched mass). The Mg and $MgCL_2$ are removed via vacuum distillation (reducing of pressure with heat to preferential vaporize volatile metal that are then condenses in a separate container).
4. The spong is further treated and allowed with other metal to be sold commercially.

The Kroll process is slow, expensive, and proposes a health/safety risk due to the high temperature vacuum distillation.

Note: alternative means of producing titanium

There are alternative means of producing titanium including the electrolysis of TiO_2 pellets via the following procedure:

1. The pellets are placed at the cathode end(usually Ti(s) or graphite) of an electrolytic cell.
2. They are dissolved in a molten $CaCl_2$(l) electrolyte.
3. The O^{2-} anions are discharged as O_2(g) at the anode(graphite).
4. The Ti^{4+} cation is reduced at the cathode resulting in a tatanium sponge

Copper Production

Cu ores often contain iron sulfides and to achieve a pure(uncontaminated) Cu product, the ores undergo the following processes :

Step 1: Concentration of ore by flotation (Figure 23.2.6.



Figure 23.2.6: Copper-sulfide foam at the flotation plant of the Prominent Hill mine in South Australia. from Wikipedia (credit: Geomarti)

Step 2: Conversion of Fe sulfide ores to Fe oxides through roasting (e.g., roasting of Chalcopyrite ore)

$$2CuFeS)2 + 3O)2 \xrightarrow{\Delta} 2FeO + 2CuS + 2SO_2 \tag{23.2.15}$$

Step 3: Smelting: mixing with coke/charcoal and heated at high temperatures (i.e 800 °C) for copper to keep Cu from remaining in sulfide form). Impurities are further removed by adding flux if not already present in ore (if gangue is acidic basic flux is added, if gangue is basic acidic flux (i.e., SiO_2) is used. Smelting separates the material to separate into 2 layers (*copper matte*: bottom layer containing molten sulfides of Fe and Cu and *silicate slag*: top layer formed by reaction of oxides of Fe, Ca, and Al w/ SiO_2).

$$FeO_{(s)} + SiO_{2(s)} \xrightarrow{\Delta} FeSiO_{3(l)} \tag{23.2.16}$$

Step 4: Conversion: Air is blown through Cu matte in a separate furnace. This converts the remaining iron sulfide to iron oxide followed by the formation of $FeSiO_3$(l) slag. The slag is poured off and the process is repeated resulting in blister copper with bubbles of SO_2(g) still present.

$$2CuS_{(l)} + 3O_{2(g)} \xrightarrow{\Delta} 2Cu_2O_{(l)} + 2SO_{2(g)} \tag{23.2.17}$$

$$2Cu_2O_{(l)} + Cu_2S_{(l)} \xrightarrow{\Delta} 6Cu(l) + SO_{2(g)} \tag{23.2.18}$$

Step 5: Blister Cu is further refined through electrolysis to achieve a high-purity Cu product.

Hydrometallurgical Process

The method of refining zinc described above is an example of a hydrometallurgical process and the hydrometallurgical process eliminates the need to control gaseous emissions that are often produced in roasting. **Hydrometallurgy** is the process of extraction and refining that involves the use of water and aqueous solutions. It is carried out at moderate temps and is generally carried out in three steps:

1. *Leaching:* metal ions are extracted from their ore by water/acids/bases/salt solutions. Redox reactions that occur are often essential.
2. *Purification and concentration:* Impurities are separated either by absorption on the surface of activated charcoal, ion exchange, or water evaporation; leaving behind a more concentrated solution.
3. *Precipitation:* the process of electrolysis is often used to precipitate the desired metal ions in an ionic solid or reduce them to their free metal.

Summary

Extractive metallurgy is the practice of removing valuable metals from an ore and refining the extracted raw metals into purer form. The field of extractive metallurgy encompasses many specialty sub-disciplines, including mineral processing, hydrometallurgy, pyrometallurgy, and electrometallurgy. Especially in hydrometallurgy, the coordination chemistry of the metals involved plays a large role in their solubility and reactivity as the ore is refined into precious metal. Many methods of extractive metallurgy may be applied to get a pure metal from its naturally occurring ore. First ores must be concentrated and separated from their earthly impurities. Concentration of ores may be achieved by froth flotation in which an ore is contained in a froth that floats at the top of a water vat. After the ore has been concentrated it must be roasted to a high temperature allowing for the desired metal to be oxidized. Once the metal is oxidized it is reduced by a reducing agent. Reduction may require the metal oxide to be heated at a high temperature. The metal must be further refined to remove all of the impurities that it may contain. Refining a metal can be accomplished by electrolysis or zone refining. Certain ores such as those of copper and titanium require special treatment before they can be refined. The extraction of iron ore is particularly important for commercial uses because of the mass production of its alloy, steel.

Problems

1. Describe 2 methods of ore concentration and list the conditions under which they are used.
2. Explain the conditions under which an ore might be roasted.
3. Explain the conditions under which an are might be electrolyzed.
4. What types of reactions occur at the cathode and anode in an electrolyzed solution?
5. How might the transition metal, zinc, be refined?
6. Explain the process of zone refining and how it may make an extracted metal more pure.
7. Explain how a change in free energy is related to extractive metallurgy. What specific process or reaction does it pertain to?
8. Give a brief explanation of why an ore might be heated to high temperatures using the principles of Thermodynamics.
9. What are the characteristics of a pyrometallurgical process and how do they compare with those of a hydrometallurgical process?
10. What are the applications of pig iron and how might it be refined to make pure iron.
11. What are the reactions that take place in the process of making steel?
12. How might an alloy of differing metals effect the properties of steel?
13. Explain 2 alternative methods of extractive metallurgy and how they differ from traditional methods.

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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:

$$\mathrm{Fe_2O_3(s) + 3C(s) \xrightarrow{\Delta} 2Fe(l) + 3CO(g)} \tag{23.3.1}$$

The actual reductant is CO, which reduces Fe_2O_3 to give Fe(l) and CO_2(g) (Equation 23.3.1); 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 23.3.1), 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.

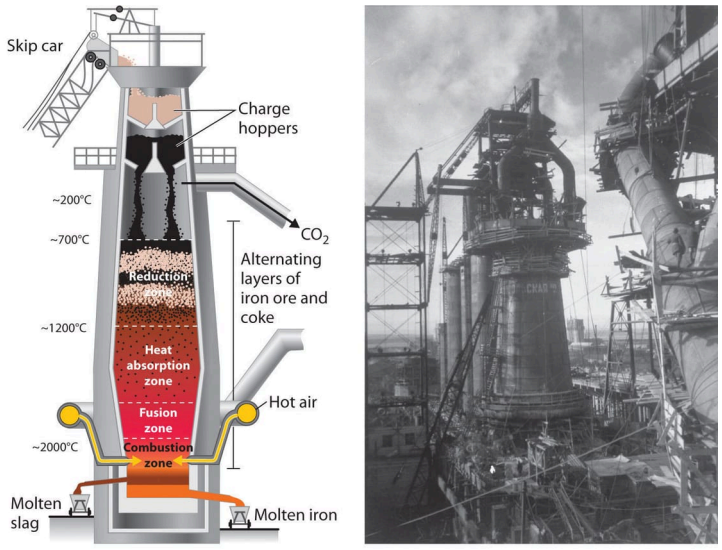


Figure 23.3.1: *A Blast Furnace for Converting Iron Oxides to Iron Metal. (a) The furnace is charged with alternating layers of iron ore (largely Fe_2O_3) and a mixture of coke (C) and limestone ($CaCO_3$). Blasting hot air into the mixture from the bottom causes it to ignite, producing CO and raising 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 23.3.2) 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.

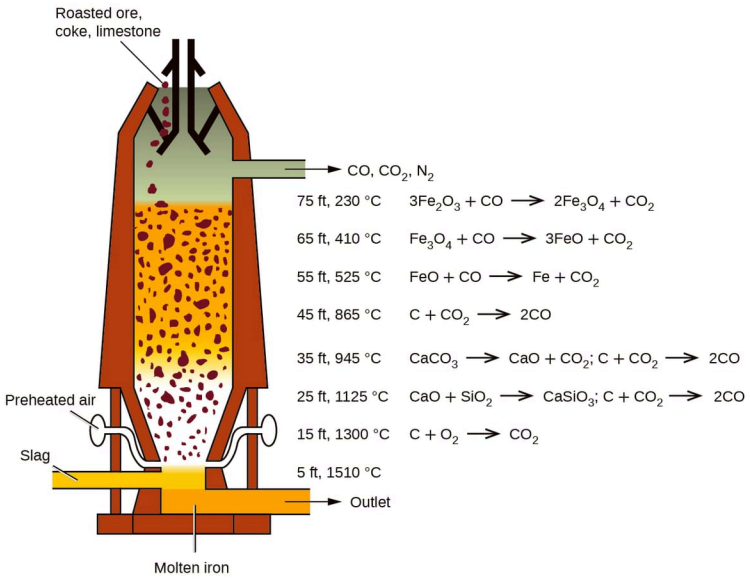


Figure 23.3.2:Within a blast furnace, different reactions occur in different temperature zones. Carbon monoxide is generated in the hotter bottom regions and rises upward to reduce the iron oxides to pure iron through a series of reactions that take place in the upper regions.

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:

$$\mathrm{CO_2}(g) + \mathrm{C}(s) \longrightarrow 2\,\mathrm{CO}(g) \tag{23.3.2}$$

The carbon monoxide serves as the reducing agent in the upper regions of the furnace. The individual reactions are indicated in Figure 23.3.2. 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:

$$\mathrm{CaO}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{CaSiO_3}(l) \tag{23.3.3}$$

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 23.3.3).



Figure 23.3.3:Molten iron is shown being cast as steel. (credit: Clint Budd)

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.

$$Mg + S \rightarrow MgS \tag{23.3.4}$$

- **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 23.3.1: 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 23.3.1).

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 (https://www.youtube.com/watch?v=nqzJk2836V8).

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23.4: First-Row Transition Metal Elements - Scandium to Manganese

Learning Objectives

- To use periodic trends to understand the chemistry of the transition metals.

As we shall see, the two heaviest members of each group usually exhibit substantial similarities in chemical behavior and are quite different from the lightest member.

Group 3 (Sc, Y, La, and Ac)

As shown in Table 23.4.1, the observed trends in the properties of the group 3 elements are similar to those of groups 1 and 2. Due to their $ns^2(n-1)d^1$ valence electron configurations, the chemistry of all four elements is dominated by the +3 oxidation state formed by losing all three valence electrons. As expected based on periodic trends, these elements are highly electropositive metals and powerful reductants, with La (and Ac) being the most reactive. In keeping with their highly electropositive character, the group 3 metals react with water to produce the metal hydroxide and hydrogen gas:

$$2M_{(s)} + 6H_2O_{(l)} \rightarrow 2M(OH)_{3(s)} + 3H_{2(g)} \tag{23.4.1}$$

The chemistry of the group 3 metals is almost exclusively that of the M^{3+} ion; the elements are powerful reductants.

Moreover, all dissolve readily in aqueous acid to produce hydrogen gas and a solution of the hydrated metal ion: $M^{3+}(aq)$.

Table 23.4.1: Some Properties of the Elements of Groups 3, 4, and 5

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
3	Sc	21	$4s^23d^1$	1.36	162	1541	2.99
	Y	39	$5s^24d^1$	1.22	180	1522	4.47
	La	57	$6s^25d^1$	1.10	183	918	6.15
	Ac	89	$7s^26d^1$	1.10	188	1051	10.07
4	Ti	22	$4s^23d^2$	1.54	147	1668	4.51
	Zr	40	$5s^24d^2$	1.33	160	1855	6.52
	Hf	72	$6s^25d^24f^{14}$	1.30	159	2233	13.31
5	V	23	$4s^23d^3$	1.63	134	1910	6.00
	Nb	41	$5s^24d^3$	1.60	146	2477	8.57
	Ta	73	$6s^25d^34f^{14}$	1.50	146	3017	16.65

The group 3 metals react with nonmetals to form compounds that are primarily ionic in character. For example, reacting group 3 metals with the halogens produces the corresponding trihalides: MX_3. The trifluorides are insoluble in water because of their high lattice energies, but the other trihalides are very soluble in water and behave like typical ionic metal halides. All group 3 elements react with air to form an oxide coating, and all burn in oxygen to form the so-called sesquioxides (M_2O_3), which react with H_2O or CO_2 to form the corresponding hydroxides or carbonates, respectively. Commercial uses of the group 3 metals are limited, but

“mischmetal,” a mixture of lanthanides containing about 40% La, is used as an additive to improve the properties of steel and make flints for cigarette lighters.

Group 4 (Ti, Zr, and Hf)

Because the elements of group 4 have a high affinity for oxygen, all three metals occur naturally as oxide ores that contain the metal in the +4 oxidation state resulting from losing all four $ns^2(n-1)d^2$ valence electrons. They are isolated by initial conversion to the tetrachlorides, as shown for Ti:

$$2FeTiO_{3(s)} + 6C_{(s)} + 7Cl_{2(g)} \rightarrow 2TiCl_{4(g)} + 2FeCl_{3(g)} + 6CO_{(g)} \tag{23.4.2}$$

followed by reduction of the tetrachlorides with an active metal such as Mg.

> The chemistry of the group 4 metals is dominated by the +4 oxidation state. Only Ti has an extensive chemistry in lower oxidation states.

In contrast to the elements of group 3, the group 4 elements have important applications. Titanium (melting point = 1668°C) is often used as a replacement for aluminum (melting point = 660°C) in applications that require high temperatures or corrosion resistance. For example, friction with the air heats the skin of supersonic aircraft operating above Mach 2.2 to temperatures near the melting point of aluminum; consequently, titanium is used instead of aluminum in many aerospace applications. The corrosion resistance of titanium is increasingly exploited in architectural applications, as shown in the chapter-opening photo. Metallic zirconium is used in UO_2-containing fuel rods in nuclear reactors, while hafnium is used in the control rods that modulate the output of high-power nuclear reactors, such as those in nuclear submarines.

Consistent with the periodic trends shown in Figure 23.2, the group 4 metals become denser, higher melting, and more electropositive down the column (Table $23.4.1$). Unexpectedly, however, the atomic radius of Hf is slightly smaller than that of Zr due to the lanthanide contraction. Because of their $ns^2(n-1)d^2$ valence electron configurations, the +4 oxidation state is by far the most important for all three metals. Only titanium exhibits a significant chemistry in the +2 and +3 oxidation states, although compounds of Ti^{2+} are usually powerful reductants. In fact, the $Ti^{2+}(aq)$ ion is such a strong reductant that it rapidly reduces water to form hydrogen gas.

Reaction of the group 4 metals with excess halogen forms the corresponding tetrahalides (MX_4), although titanium, the lightest element in the group, also forms dihalides and trihalides (X is not F). The covalent character of the titanium halides increases as the oxidation state of the metal increases because of increasing polarization of the anions by the cation as its charge-to-radius ratio increases. Thus $TiCl_2$ is an ionic salt, whereas $TiCl_4$ is a volatile liquid that contains tetrahedral molecules. All three metals react with excess oxygen or the heavier chalcogens (Y) to form the corresponding dioxides (MO_2) and dichalcogenides (MY_2). Industrially, TiO_2, which is used as a white pigment in paints, is prepared by reacting $TiCl_4$ with oxygen at high temperatures:

$$TiCl_{4(g)} + O_{2(g)} \rightarrow TiO_{2(s)} + 2Cl_{2(g)} \tag{23.4.3}$$

The group 4 dichalcogenides have unusual layered structures with no M–Y bonds holding adjacent sheets together, which makes them similar in some ways to graphite (Figure $23.4.1$). The group 4 metals also react with hydrogen, nitrogen, carbon, and boron to form hydrides (such as TiH_2), nitrides (such as TiN), carbides (such as TiC), and borides (such as TiB_2), all of which are hard, high-melting solids. Many of these binary compounds are nonstoichiometric and exhibit metallic conductivity.

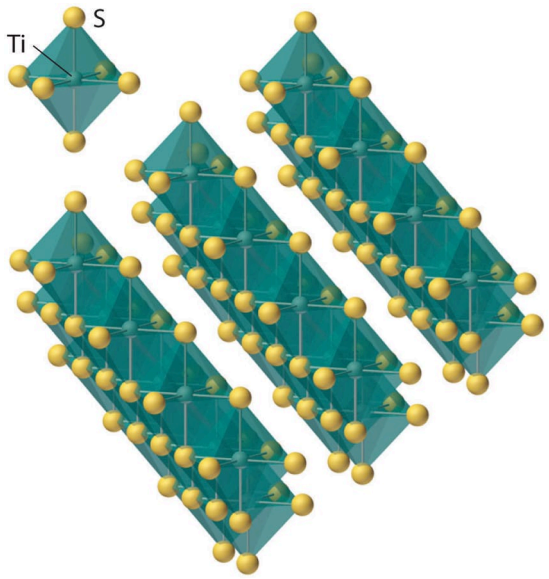


Figure 23.4.1: The Layered Structure of TiS_2. Each titanium atom is surrounded by an octahedral arrangement of six sulfur atoms that are shared to form extended layers of atoms. Because the layers are held together by only van der Waals forces between adjacent sulfur atoms, rather than covalent bonds, the layers slide past one another relatively easily when a mechanical stress is applied.

Group 5 (V, Nb, and Ta)

Like the group 4 elements, all group 5 metals are normally found in nature as oxide ores that contain the metals in their highest oxidation state (+5). Because of the lanthanide contraction, the chemistry of Nb and Ta is so similar that these elements are usually found in the same ores.

Three-fourths of the vanadium produced annually is used in the production of steel alloys for springs and high-speed cutting tools. Adding a small amount of vanadium to steel results in the formation of small grains of V_4C_3, which greatly increase the strength and resilience of the metal, especially at high temperatures. The other major use of vanadium is as V_2O_5, an important catalyst for the industrial conversion of SO_2 to SO_3 in the contact process for the production of sulfuric acid. In contrast, Nb and Ta have only limited applications, and they are therefore produced in relatively small amounts. Although niobium is used as an additive in certain stainless steels, its primary application is in superconducting wires such as Nb_3Zr and Nb_3Ge, which are used in superconducting magnets for the magnetic resonance imaging of soft tissues. Because tantalum is highly resistant to corrosion, it is used as a liner for chemical reactors, in missile parts, and as a biologically compatible material in screws and pins for repairing fractured bones.

> The chemistry of the two heaviest group 5 metals (Nb and Ta) is dominated by the +5 oxidation state. The chemistry of the lightest element (V) is dominated by lower oxidation states, especially +4.

As indicated in Table 23.4.1, the trends in properties of the group 5 metals are similar to those of group 4. Only vanadium, the lightest element, has any tendency to form compounds in oxidation states lower than +5. For example, vanadium is the only element in the group that forms stable halides in the lowest oxidation state (+2). All three metals react with excess oxygen, however, to produce the corresponding oxides in the +5 oxidation state (M_2O_5), in which polarization of the oxide ions by the high-oxidation-state metal is so extensive that the compounds are primarily covalent in character. Vanadium–oxygen species provide a classic example of the effect of increasing metal oxidation state on the protonation state of a coordinated water molecule: vanadium(II) in water exists as the violet hydrated ion $[V(H_2O)_6]^{2+}$; the blue-green $[V(H_2O)_6]^{3+}$ ion is acidic, dissociating to form small amounts of the $[V(H_2O)_5(OH)]^{2+}$ ion and a proton; and in water, vanadium(IV) forms the blue vanadyl ion $[(H_2O)_4VO]^{2+}$, which contains a formal V=O bond (Figure 23.4.2). Consistent with its covalent character, V_2O_5 is acidic, dissolving in base to give the vanadate ion ($[VO_4]^{3-}$), whereas both Nb_2O_5 and Ta_2O_5 are comparatively inert. Oxides of these metals in lower oxidation states tend to be nonstoichiometric.

Because vanadium ions with different oxidation states have different numbers of d electrons, aqueous solutions of the ions have different colors: in acid V(V) forms the pale yellow $[VO_2]^+$ ion; V(IV) is the blue vanadyl ion $[VO]^{2+}$; and V(III) and V(II) exist as the

hydrated V^{3+} (blue-green) and V^{2+} (violet) ions, respectively.

Although group 5 metals react with the heavier chalcogens to form a complex set of binary chalcogenides, the most important are the dichalcogenides (MY_2), whose layered structures are similar to those of the group 4 dichalcogenides. The elements of group 5 also form binary nitrides, carbides, borides, and hydrides, whose stoichiometries and properties are similar to those of the corresponding group 4 compounds. One such compound, tantalum carbide (TiC), has the highest melting point of any compound known (3738°C); it is used for the cutting edges of high-speed machine tools.

Group 6 (Cr, Mo, and W)

As an illustration of the trend toward increasing polarizability as we go from left to right across the d block, in group 6 we first encounter a metal (Mo) that occurs naturally as a sulfide ore rather than as an oxide. Molybdenite (MoS_2) is a soft black mineral that can be used for writing, like PbS and graphite. Because of this similarity, people long assumed that these substances were all the same. In fact, the name molybdenum is derived from the Greek molybdos, meaning “lead.” More than 90% of the molybdenum produced annually is used to make steels for cutting tools, which retain their sharp edge even when red hot. In addition, molybdenum is the only second- or third-row transition element that is essential for humans. The major chromium ore is chromite ($FeCr_2O_4$), which is oxidized to the soluble $[CrO_4]^{2-}$ ion under basic conditions and reduced successively to Cr_2O_3 and Cr with carbon and aluminum, respectively. Pure chromium can be obtained by dissolving Cr_2O_3 in sulfuric acid followed by electrolytic reduction; a similar process is used for electroplating metal objects to give them a bright, shiny, protective surface layer. Pure tungsten is obtained by first converting tungsten ores to WO_3, which is then reduced with hydrogen to give the metal.

The metals become increasing polarizable across the d block.

Consistent with periodic trends, the group 6 metals are slightly less electropositive than those of the three preceding groups, and the two heaviest metals are essentially the same size because of the lanthanide contraction (Table 23.4.2). All three elements have a total of six valence electrons, resulting in a maximum oxidation state of +6. Due to extensive polarization of the anions, compounds in the +6 oxidation state are highly covalent. As in groups 4 and 5, the lightest element exhibits variable oxidation states, ranging from Cr^{2+}, which is a powerful reductant, to CrO_3, a red solid that is a powerful oxidant. For Mo and W, the highest oxidation state (+6) is by far the most important, although compounds in the +4 and +5 oxidation states are known.

Table 23.4.2: Some Properties of the Elements of Groups 6 and 7

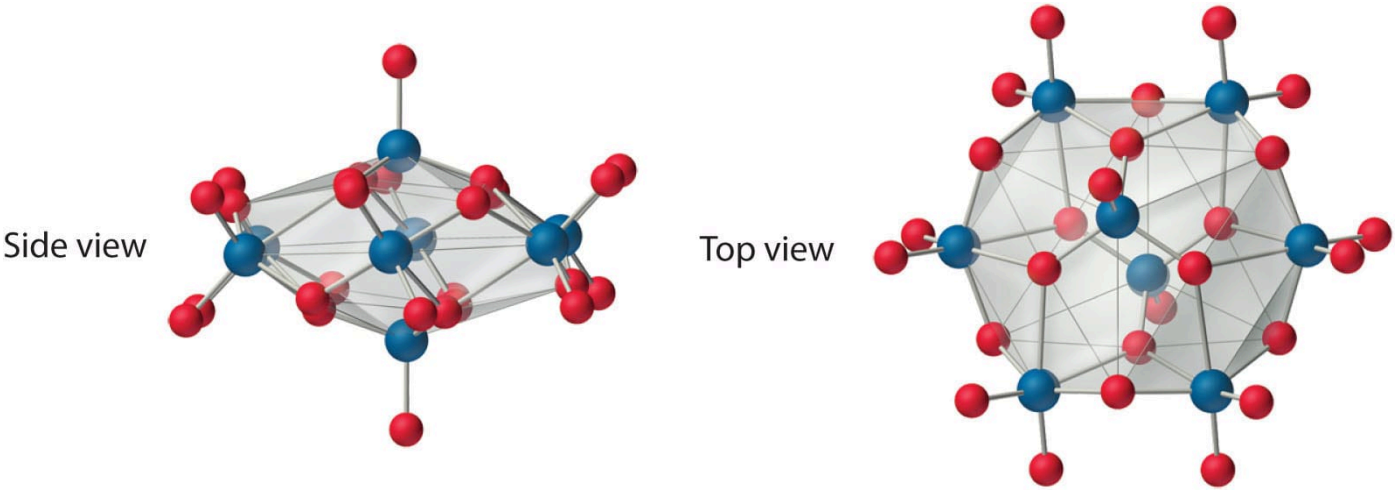
Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
6	Cr	24	$4s^1 3d^5$	1.66	128	1907	7.15
	Mo	42	$5s^1 4d^5$	2.16	139	2623	10.20
	W	74	$6s^2 5d^4 4f^{14}$	1.70	139	3422	19.30
7	Mn	25	$4s^2 3d^5$	1.55	127	1246	7.30
	Tc	43	$5s^2 4d^5$	2.10	136	2157	11.50
	Re	75	$6s^2 5d^5 4f^{14}$	1.90	137	3186	20.80

The chemistry of the two heaviest group 6 metals (Mo and W) is dominated by the +6 oxidation state. The chemistry of the lightest element (Cr) is dominated by lower oxidation states.

As observed in previous groups, the group 6 halides become more covalent as the oxidation state of the metal increases: their volatility increases, and their melting points decrease. Recall that as the electronegativity of the halogens decreases from F to I, they are less able to stabilize high oxidation states; consequently, the maximum oxidation state of the corresponding metal halides decreases. Thus all three metals form hexafluorides, but CrF_6 is unstable at temperatures above –100°C, whereas MoF_6 and WF_6 are stable. Consistent with the trend toward increased stability of the highest oxidation state for the second- and third-

row elements, the other halogens can oxidize chromium to only the trihalides, CrX_3 (X is Cl, Br, or I), while molybdenum forms $MoCl_5$, $MoBr_4$, and MoI_3, and tungsten gives WCl_6, WBr_5, and WI_4.

Both Mo and W react with oxygen to form the covalent trioxides (MoO_3 and WO_3), but Cr reacts to form only the so-called sesquioxide (Cr_2O_3). Chromium will form CrO_3, which is a highly toxic compound that can react explosively with organic materials. All the trioxides are acidic, dissolving in base to form the corresponding oxoanions ($[MO_4]^{2-}$). Consistent with periodic trends, the sesquioxide of the lightest element in the group (Cr_2O_3) is amphoteric. The aqueous chemistry of molybdate and tungstate is complex, and at low pH they form a series of polymeric anions called isopolymetallates, such as the $[Mo_8O_{26}]^{4-}$ ion, whose structure is as follows:



An isopolymolybdate cluster. The $[Mo_8O_{26}]^{4-}$ ion, shown here in both side and top views, is typical of the oxygen-bridged clusters formed by Mo(VI) and W(VI) in aqueous solution.

Reacting molybdenum or tungsten with heavier chalcogens gives binary chalcogenide phases, most of which are nonstoichiometric and electrically conducting. One of the most stable is MoS_2; it has a layered structure similar to that of TiS_2 (Figure 23.4.1), in which the layers are held together by only weak van der Waals forces, which allows them to slide past one another rather easily. Consequently, both MoS_2 and WS_2 are used as lubricants in a variety of applications, including automobile engines. Because tungsten itself has an extraordinarily high melting point (3380°C), lubricants described as containing "liquid tungsten" actually contain a suspension of very small WS_2 particles.

As in groups 4 and 5, the elements of group 6 form binary nitrides, carbides, and borides whose stoichiometries and properties are similar to those of the preceding groups. Tungsten carbide (WC), one of the hardest compounds known, is used to make the tips of drill bits.

Group 7 (Mn, Tc, and Re)

Continuing across the periodic table, we encounter the group 7 elements (Table 23.4.2). One group 7 metal (Mn) is usually combined with iron in an alloy called ferromanganese, which has been used since 1856 to improve the mechanical properties of steel by scavenging sulfur and oxygen impurities to form MnS and MnO. Technetium is named after the Greek technikos, meaning "artificial," because all its isotopes are radioactive. One isotope, ^{99m}Tc (m for metastable), has become an important biomedical tool for imaging internal organs. Because of its scarcity, Re is one of the most expensive elements, and its applications are limited. It is, however, used in a bimetallic Pt/Re catalyst for refining high-octane gasoline.

All three group 7 elements have seven valence electrons and can form compounds in the +7 oxidation state. Once again, the lightest element exhibits multiple oxidation states. Compounds of Mn in oxidation states ranging from −3 to +7 are known, with the most common being +2 and +4 (Figure 23.4.3). In contrast, compounds of Tc and Re in the +2 oxidation state are quite rare. Because the electronegativity of Mn is anomalously low, elemental manganese is unusually reactive. In contrast, the chemistry of Tc is similar to that of Re because of their similar size and electronegativity, again a result of the lanthanide contraction. Due to the stability of the half-filled $3d^5$ electron configuration, the aqueous Mn^{3+} ion, with a $3d^4$ valence electron configuration, is a

potent oxidant that is able to oxidize water. It is difficult to generalize about other oxidation states for Tc and Re because their stability depends dramatically on the nature of the compound.

Like vanadium, compounds of manganese in different oxidation states have different numbers of d electrons, which leads to compounds with different colors: the $Mn^{2+}(aq)$ ion is pale pink; $Mn(OH)_3$, which contains Mn(III), is a dark brown solid; MnO_2, which contains Mn(IV), is a black solid; and aqueous solutions of Mn(VI) and Mn(VII) contain the green manganate ion $[MnO_4]^{2-}$ and the purple permanganate ion $[MnO_4]^-$, respectively.

Consistent with higher oxidation states being more stable for the heavier transition metals, reacting Mn with F_2 gives only MnF_3, a high-melting, red-purple solid, whereas Re reacts with F_2 to give ReF_7, a volatile, low-melting, yellow solid. Again, reaction with the less oxidizing, heavier halogens produces halides in lower oxidation states. Thus reaction with Cl_2, a weaker oxidant than F_2, gives $MnCl_2$ and $ReCl_6$. Reaction of Mn with oxygen forms only Mn_3O_4, a mixed-valent compound that contains two Mn(II) and one Mn(III) per formula unit and is similar in both stoichiometry and structure to magnetite (Fe_3O_4). In contrast, Tc and Re form high-valent oxides, the so-called heptoxides (M_2O_7), consistent with the increased stability of higher oxidation states for the second and third rows of transition metals. Under forced conditions, manganese will form Mn_2O_7, an unstable, explosive, green liquid. Also consistent with this trend, the permanganate ion $[MnO_4]^{2-}$ is a potent oxidant, whereas $[TcO_4]^-$ and $[ReO_4]^-$ are much more stable. Both Tc and Re form disulfides and diselenides with layered structures analogous to that of MoS_2, as well as more complex heptasulfides (M_2S_7). As is typical of the transition metals, the group 7 metals form binary nitrides, carbides, and borides that are generally stable at high temperatures and exhibit metallic properties.

> The chemistry of the group 7 metals (Mn, Tc, and Re) is dominated by lower oxidation states. Compounds in the maximum possible oxidation state (+7) are readily reduced.

Groups 8, 9, and 10

In many older versions of the periodic table, groups 8, 9, and 10 were combined in a single group (group VIII) because the elements of these three groups exhibit many horizontal similarities in their chemistry, in addition to the similarities within each column. In part, these horizontal similarities are due to the fact that the ionization potentials of the elements, which increase slowly but steadily across the d block, have now become so large that the oxidation state corresponding to the formal loss of all valence electrons is encountered only rarely (group 8) or not at all (groups 9 and 10). As a result, the chemistry of all three groups is dominated by intermediate oxidation states, especially +2 and +3 for the first-row metals (Fe, Co, and Ni). The heavier elements of these three groups are called precious metals because they are rather rare in nature and mostly chemically inert.

> The chemistry of groups 8, 9, and 10 is dominated by intermediate oxidation states such as +2 and +3.

Group 8 (Fe, Ru, and Os)

The chemistry of group 8 is dominated by iron, whose high abundance in Earth's crust is due to the extremely high stability of its nucleus. Ruthenium and osmium, on the other hand, are extremely rare elements, with terrestrial abundances of only about 0.1 ppb and 5 ppb, respectively, and they were not discovered until the 19th century. Because of the high melting point of iron (1538°C), early humans could not use it for tools or weapons. The advanced techniques needed to work iron were first developed by the Hittite civilization in Asia Minor sometime before 2000 BC, and they remained a closely guarded secret that gave the Hittites military supremacy for almost a millennium. With the collapse of the Hittite civilization around 1200 BC, the technology became widely distributed, however, leading to the Iron Age.

Group 9 (Co, Rh, and Ir)

Cobalt is one of the least abundant of the first-row transition metals. Its oxide ores, however, have been used in glass and pottery for thousands of years to produce the brilliant color known as "cobalt blue," and its compounds are consumed in large quantities in the paint and ceramics industries. The heavier elements of group 9 are also rare, with terrestrial abundances of less than 1 ppb; they are generally found in combination with the heavier elements of groups 8 and 10 in Ni–Cu–S ores.

Group 10 (Ni, Pd, and Pt)

Nickel silicates are easily processed; consequently, nickel has been known and used since antiquity. In fact, a 75:25 Cu:Ni alloy was used for more than 2000 years to mint “silver” coins, and the modern US nickel uses the same alloy. In contrast to nickel, palladium and platinum are rare (their terrestrial abundance is about 10–15 ppb), but they are at least an order of magnitude more abundant than the heavier elements of groups 8 and 9. Platinum and palladium are used in jewelry, the former as the pure element and the latter as the Pd/Au alloy known as white gold.



Over 2000 years ago, the Bactrian civilization in Western Asia used a 75:25 alloy of copper and nickel for its coins. A modern US nickel has the same composition, but a modern Canadian nickel is nickel-plated steel and contains only 2.5% nickel by mass.

Trends in Group 8, 9, and 10

Some properties of the elements in groups 8–10 are summarized in Table 23.4.3. As in earlier groups, similarities in size and electronegativity between the two heaviest members of each group result in similarities in chemistry. We are now at the point in the d block where there is no longer a clear correlation between the valence electron configuration and the preferred oxidation state. For example, all the elements of group 8 have eight valence electrons, but only Ru and Os have any tendency to form compounds in the +8 oxidation state, and those compounds are powerful oxidants. The predominant oxidation states for all three group 8 metals are +2 and +3. Although the elements of group 9 possess a total of nine valence electrons, the +9 oxidation state is unknown for these elements, and the most common oxidation states in the group are +3 and +1. Finally, the elements of group 10 all have 10 valence electrons, but all three elements are normally found in the +2 oxidation state formed by losing the ns2 valence electrons. In addition, Pd and Pt form numerous compounds and complexes in the +4 oxidation state.

Table 23.4.3: Some Properties of the Elements of Groups 8, 9, and 10

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
8	Fe	26	$4s^2 3d^6$	1.83	126	1538	7.87
	Ru	44	$5s^1 4d^7$	2.20	134	2334	12.10
	Os	76	$6s^2 5d^6 4f^{14}$	2.20	135	3033	22.59
9	Co	27	$4s^2 3d^7$	1.88	125	1495	8.86
	Rh	45	$5s^1 4d^8$	2.28	134	1964	12.40

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
	Ir	77	$6s^2 5d^7 4f^{14}$	2.20	136	2446	22.50
10	Ni	28	$4s^2 3d^8$	1.91	124	1455	8.90
	Pd	46	$4d^{10}$	2.20	137	1555	12.00
	Pt	78	$6s^2 5d^8 4f^{14}$	2.20	139	1768	21.50

We stated that higher oxidation states become less stable as we go across the d-block elements and more stable as we go down a group. Thus Fe and Co form trifluorides, but Ni forms only the difluoride NiF_2. In contrast to Fe, Ru and Os form a series of fluorides up to RuF_6 and OsF_7. The hexafluorides of Rh and Ir are extraordinarily powerful oxidants, and Pt is the only element in group 10 that forms a hexafluoride. Similar trends are observed among the oxides. For example, Fe forms only FeO, Fe_2O_3, and the mixed-valent Fe_3O_4 (magnetite), all of which are nonstoichiometric. In contrast, Ru and Os form the dioxides (MO_2) and the highly toxic, volatile, yellow tetroxides, which contain formal M=O bonds. As expected for compounds of metals in such high oxidation states, the latter are potent oxidants. The tendency of the metals to form the higher oxides decreases rapidly as we go farther across the d block.

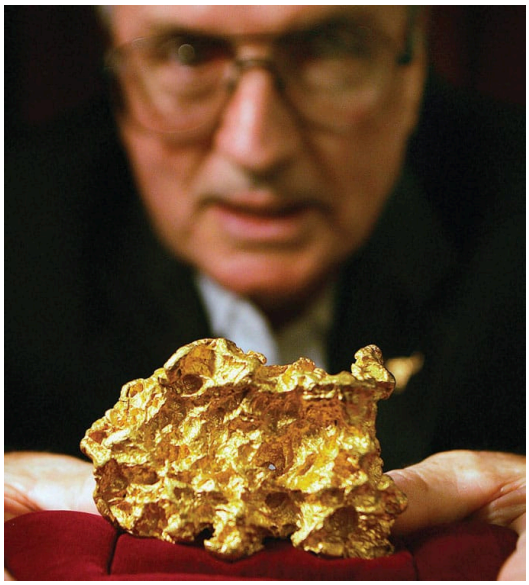
Higher oxidation states become less stable across the d-block, but more stable down a group.

Reactivity with the heavier chalcogens is rather complex. Thus the oxidation state of Fe, Ru, Os, Co, and Ni in their disulfides is +2 because of the presence of the disulfide ion (S_2^{2-}), but the disulfides of Rh, Ir, Pd, and Pt contain the metal in the +4 oxidation state together with sulfide ions (S^{2-}). This combination of highly charged cations and easily polarized anions results in substances that are not simple ionic compounds and have significant covalent character.

The groups 8–10 metals form a range of binary nitrides, carbides, and borides. By far the most important of these is cementite (Fe_3C), which is used to strengthen steel. At high temperatures, Fe_3C is soluble in iron, but slow cooling causes the phases to separate and form particles of cementite, which gives a metal that retains much of its strength but is significantly less brittle than pure iron. Palladium is unusual in that it forms a binary hydride with the approximate composition $PdH_{0.5}$. Because the H atoms in the metal lattice are highly mobile, thin sheets of Pd are highly permeable to H_2 but essentially impermeable to all other gases, including He. Consequently, diffusion of H_2 through Pd is an effective method for separating hydrogen from other gases.

Group 11 (Cu, Ag, and Au)

The coinage metals—copper, silver, and gold—occur naturally (like the gold nugget shown here); consequently, these were probably the first metals used by ancient humans. For example, decorative gold artifacts dating from the late Stone Age are known, and some gold Egyptian coins are more than 5000 yr old. Copper is almost as ancient, with objects dating to about 5000 BC. Bronze, an alloy of copper and tin that is harder than either of its constituent metals, was used before 3000 BC, giving rise to the Bronze Age. Deposits of silver are much less common than deposits of gold or copper, yet by 3000 BC, methods had been developed for recovering silver from its ores, which allowed silver coins to be widely used in ancient times.



This 1 kg gold nugget was found in Australia; in 2005, it was for sale in Hong Kong at an asking price of more than US$64,000.

Deposits of gold and copper are widespread and numerous, and for many centuries it was relatively easy to obtain large amounts of the pure elements. For example, a single gold nugget discovered in Australia in 1869 weighed more than 150 lb. Because the demand for these elements has outstripped their availability, methods have been developed to recover them economically from even very low-grade ores (as low as 1% Cu content for copper) by operating on a vast scale, as shown in the photo of an open-pit copper mine. Copper is used primarily to manufacture electric wires, but large quantities are also used to produce bronze, brass, and alloys for coins. Much of the silver made today is obtained as a by-product of the manufacture of other metals, especially Cu, Pb, and Zn. In addition to its use in jewelry and silverware, silver is used in Ag/Zn and Ag/Cd button batteries. Gold is typically found either as tiny particles of the pure metal or as gold telluride ($AuTe_2$). It is used as a currency reserve, in jewelry, in the electronics industry for corrosion-free contacts, and, in very thin layers, as a reflective window coating that minimizes heat transfer.



The Chuquicamata copper mine in northern Chile, the world's largest open-pit copper mine, is 4.3 km long, 3 km wide, and 825 m deep. Each gigantic truck in the foreground (and barely visible in the lower right center) can hold 330 metric tn (330,000 kg) of copper ore.

Some properties of the coinage metals are listed in Table 23.4.4. The electronegativity of gold (χ = 2.40) is close to that of the

nonmetals sulfur and iodine, which suggests that the chemistry of gold should be somewhat unusual for a metal. The coinage metals have the highest electrical and thermal conductivities of all the metals, and they are also the most ductile and malleable. With an $ns^1(n-1)d^{10}$ valence electron configuration, the chemistry of these three elements is dominated by the +1 oxidation state due to losing the single ns electron. Higher oxidation states are also known, however: +2 is common for Cu and, to a lesser extent, Ag, and +3 for Au because of the relatively low values of the second and (for Au) third ionization energies. All three elements have significant electron affinities due to the half-filled ns orbital in the neutral atoms. As a result, gold reacts with powerful reductants like Cs and solutions of the alkali metals in liquid ammonia to produce the gold anion Au^- with a $6s^25d^{10}$ valence electron configuration.

Table 23.4.4: Some Properties of the Elements of Groups 11 and 12

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
11	Cu	29	$4s^13d^{10}$	1.90	128	1085	8.96
	Ag	47	$5s^14d^{10}$	1.93	144	962	10.50
	Au	79	$6s^15d^{10}4f^{14}$	2.40	144	1064	19.30
12	Zn	30	$4s^23d^{10}$	1.65	134	420	7.13
	Cd	48	$5s^24d^{10}$	1.69	149	321	8.69
	Hg	80	$6s^25d^{10}4f^{14}$	1.90	151	–38.8	13.53

All group 11 elements are relatively unreactive, and their reactivity decreases from Cu to Au. Hence they are noble metals that are particularly well suited for use in coins and jewelry. Copper reacts with O_2 at high temperatures to produce Cu_2O and with sulfur to form Cu_2S. Neither silver nor gold reacts directly with oxygen, although oxides of these elements can be prepared by other routes. Silver reacts with sulfur compounds to form the black Ag_2S coating known as tarnish. Gold is the only metal that does not react with sulfur; it also does not react with nitrogen, carbon, or boron. All the coinage metals do, however, react with oxidizing acids. Thus both Cu and Ag dissolve in HNO_3 and in hot concentrated H_2SO_4, while Au dissolves in the 3:1 HCl:HNO_3 mixture known as aqua regia. Furthermore, all three metals dissolve in basic cyanide solutions in the presence of oxygen to form very stable $[M(CN)_2]^-$ ions, a reaction that is used to separate gold from its ores.

> Although the most important oxidation state for group 11 is +1, the elements are relatively unreactive, with reactivity decreasing from Cu to Au.

All the monohalides except CuF and AuF are known (including AgF). Once again, iodine is unable to stabilize the higher oxidation states (Au^{3+} and Cu^{2+}). Thus all the copper(II) halides except the iodide are known, but the only dihalide of silver is AgF_2. In contrast, all the gold trihalides (AuX_3) are known, again except the triiodide. No binary nitrides, borides, or carbides are known for the group 11 elements.

Group 12 (Zn, Cd, and Hg)

We next encounter the group 12 elements. Because none of the elements in group 12 has a partially filled (n – 1)d subshell, they are not, strictly speaking, transition metals. Nonetheless, much of their chemistry is similar to that of the elements that immediately precede them in the d block. The group 12 metals are similar in abundance to those of group 11, and they are almost always found in combination with sulfur. Because zinc and cadmium are chemically similar, virtually all zinc ores contain significant amounts of cadmium. All three metals are commercially important, although the use of Cd is restricted because of its toxicity. Zinc is used for corrosion protection, in batteries, to make brass, and, in the form of ZnO, in the production of rubber and paints. Cadmium is used as the cathode in rechargeable NiCad batteries. Large amounts of mercury are used in the production of chlorine and NaOH by the chloralkali process, while smaller amounts are consumed in mercury-vapor streetlights and mercury batteries.

As shown in Table 23.4.4, the group 12 metals are significantly more electropositive than the elements of group 11, and they therefore have less noble character. They also have much lower melting and boiling points than the preceding transition metals. In contrast to trends in the preceding groups, Zn and Cd are similar to each other, but very different from the heaviest element (Hg). In particular, Zn and Cd are rather active metals, whereas mercury is not. Because mercury, the only metal that is a liquid at room

temperature, can dissolve many metals by forming amalgams, medieval alchemists especially valued it when trying to transmute base metals to gold and silver. All three elements in group 12 have $ns^2(n-1)d^{10}$ valence electron configurations; consequently, the +2 oxidation state, corresponding to losing the two ns electrons, dominates their chemistry. In addition, mercury forms a series of compounds in the +1 oxidation state that contain the diatomic mercurous ion Hg_2^{2+}.

> The most important oxidation state for group 12 is +2; the metals are significantly more electropositive than the group 11 elements, so they are less noble.

All the possible group 12 dihalides (MX_2) are known, and they range from ionic (the fluorides) to highly covalent (such as $HgCl_2$). The highly covalent character of many mercuric and mercurous halides is surprising given the large size of the cations, and this has been attributed to the existence of an easily distorted $5d^{10}$ subshell. Zinc and cadmium react with oxygen to form amphoteric MO, whereas mercury forms HgO only within a narrow temperature range (350–400°C). Whereas zinc and cadmium dissolve in mineral acids such as HCl with the evolution of hydrogen, mercury dissolves only in oxidizing acids such as HNO_3 and H_2SO_4. All three metals react with sulfur and the other chalcogens to form the binary chalcogenides; mercury also has an extraordinarily high affinity for sulfur.

Example 23.4.1

For each reaction, explain why the indicated products form.

a. $TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(aq)$
b. $WO_3(s) + 3C(s) + 3Cl_2(g) \xrightarrow{\Delta} WCl_6(s) + 3CO(g)$
c. $Sc_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Sc(OH)_4]^-(aq)$
d. $2KMnO_4(aq) + 2H_2SO_4(l) \rightarrow Mn_2O_7(l) + 2KHSO_4(soln) + H_2O(soln)$
e. $4CrCl_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Cr^{3+}(aq) + 8Cl^-(aq) + 2H_2O(l)$

Given: balanced chemical equation

Asked for: why the indicated products form

Strategy:

Refer to the periodic trends in this section.

Solution:

a. The most stable oxidation state for Ti is +4, and neither reactant is a particularly strong oxidant or reductant; hence a redox reaction is unlikely. Similarly, neither reactant is a particularly strong acid or base, so an acid–base reaction is unlikely. Because $TiCl_4$ contains Ti in a relatively high oxidation state (+4), however, it is likely to be rather covalent in character, with reactivity similar to that of a semimetal halide such as $SiCl_4$. Covalent halides tend to hydrolyze in water to produce the hydrohalic acid and either the oxide of the other element or a species analogous to an oxoacid.
b. This reaction involves the oxide of a group 6 metal in its highest oxidation state (WO_3) and two elements, one of which is a reductant (C) and the other an oxidant (Cl_2). Consequently, some sort of redox reaction will occur. Carbon can certainly react with chlorine to form CCl_4, and WO_3 is a potential source of oxygen atoms that can react with carbon to produce CO, which is very stable. If CO is one of the products, then it seems likely that the other product will contain the metal and chlorine. The most likely combination is WCl_6 (leaving the oxidation state of the metal unchanged).
c. One of the reactants is a strong base (OH^-), so an acid–base reaction is likely if the other reactant is acidic. Because oxides like Sc_2O_3, in which the metal is in an intermediate oxidation state, are often amphoteric, we expect Sc_2O_3 to dissolve in base to form a soluble hydroxide complex.
d. Concentrated sulfuric acid is both an oxidant and a strong acid that tends to protonate and dehydrate other substances. The permanganate ion already contains manganese in its highest possible oxidation state (+7), so it cannot be oxidized further. A redox reaction is impossible, which leaves an acid–base reaction as the most likely alternative. Sulfuric acid is likely to protonate the terminal oxygen atoms of permanganate, allowing them to be lost as water.

e. Molecular oxygen is an oxidant, so a redox reaction is likely if the other reactant can be oxidized. Because chromous chloride contains chromium in its lowest accessible oxidation state, a redox reaction will occur in which Cr^{2+} ions are oxidized and O_2 is reduced. In the presence of protons, the reduction product of O_2 is water, so we need to determine only the identity of the oxidation product of Cr^{2+}. Chromium forms compounds in two common higher oxidation states: the Cr^{3+} ion, which is the most stable, and the $[Cr_2O_7]^{2-}$ ion, which is a more powerful oxidant than O_2. We therefore predict that the reaction will form $Cr^{3+}(aq)$ and water.

Exercise 23.4.1

Predict the products of each reactions and then balance each chemical equation.

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \xrightarrow{H^+}$
b. $Na_2Cr_2O_7(aq) + H_2SO_4(l) \rightarrow$
c. $FeBr_2(aq) + O_2(g) \xrightarrow{H^+}$
d. $VBr_4(l) + H_2O(l) \rightarrow$
e. $ZrO_2(s) + C(s) + Cl_2(g) \xrightarrow{\Delta}$

Answer

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \xrightarrow{H^+} Cr^{3+}(aq) + Fe^{2+}(aq)$
b. $Na_2Cr_2O_7(aq) + 2H_2SO_4(l) \rightarrow 2NaHSO_4(soln) + H_2O(soln) + 2CrO_3(s)$
c. $4FeBr_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) + 8Br^-(aq)$
d. $VBr_4(l) + H_2O(l) \rightarrow VO^{2+}(aq) + 4Br^-(aq) + 2H^+(aq)$
e. $ZrO_2(s) + 2C(s) + 2Cl_2(g) \xrightarrow{\Delta} ZrCl_4(s) + 2CO(g)$

Summary

The elements tend to become more polarizable going across the d block and higher oxidation states become less stable; higher oxidation states become more stable going down a group. The group 3 transition metals are highly electropositive metals and powerful reductants. They react with nonmetals to form compounds that are largely ionic and with oxygen to form sesquioxides (M_2O_3). The group 4 metals also have a high affinity for oxygen. In their reactions with halogens, the covalent character of the halides increases as the oxidation state of the metal increases because the high charge-to-radius ratio causes extensive polarization of the anions. The dichalcogenides have layered structures similar to graphite, and the hydrides, nitrides, carbides, and borides are all hard, high-melting-point solids with metallic conductivity. The group 5 metals also have a high affinity for oxygen. Consistent with periodic trends, only the lightest (vanadium) has any tendency to form compounds in oxidation states lower than +5. The oxides are sufficiently polarized to make them covalent in character. These elements also form layered chalcogenides, as well as nitrides, carbides, borides, and hydrides that are similar to those of the group 4 elements. As the metals become more polarizable across the row, their affinity for oxygen decreases. The group 6 metals are less electropositive and have a maximum oxidation state of +6, making their compounds in high oxidation states largely covalent in character. As the oxidizing strength of the halogen decreases, the maximum oxidation state of the metal also decreases. All three trioxides are acidic, but Cr_2O_3 is amphoteric. The chalcogenides of the group 6 metals are generally nonstoichiometric and electrically conducting, and these elements also form nitrides, carbides, and borides that are similar to those in the preceding groups. The metals of group 7 have a maximum oxidation state of +7, but the lightest element, manganese, exhibits an extensive chemistry in lower oxidation states. As with the group 6 metals, reaction with less oxidizing halogens produces metals in lower oxidation states, and disulfides and diselenides of Tc and Re have layered structures. The group 7 metals also form nitrides, carbides, and borides that are stable at high temperatures and have metallic properties. In groups 8, 9, and 10, the ionization potentials of the elements are so high that the oxidation state corresponding to the formal loss of all valence electrons is encountered rarely (group 8) or not at all (groups 9 and 10). Compounds of group 8 metals in their highest oxidation state are powerful oxidants. The reaction of metals in groups 8, 9, and 10 with the chalcogens is complex, and these elements form a range of binary nitrides, carbides, and borides. The coinage metals (group 11) have the highest electrical and thermal conductivities and are the most ductile and malleable of the metals. Although they are relatively unreactive, they form halides but not nitrides, borides, or carbides. The group 12 elements, whose chemistry is dominated by the +2 oxidation state, are almost always found in nature combined

with sulfur. Mercury is the only metal that is a liquid at room temperature, and it dissolves many metals to form amalgams. The group 12 halides range from ionic to covalent. These elements form chalcogenides and have a high affinity for soft ligands.

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23.5: The Iron Triad: Iron, Cobalt, and Nickel

The Iron Triad is composed of three elements: iron (Fe), cobalt (Co), and nickel (Ni), which share similar chemical and physical characteristics. They are found adjacent to each other in period 4 of the periodic table.

Introduction

The Iron Triad is known for possessing ferromagnetic elements similar to gadolinium (Gd), and neodymium (Nd). These types of ferromagnetic elements have the ability to create a large magnetic pole due to their unpaired electrons. When one of these elements is inside an environment where the temperature is at its individual **Curie Point** (T_C), however, the specific paramagnetic lining of atoms is broken down by the energy within the element and ferromagnetism is lost. The (T_C)'s for iron, cobalt, and nickel are 768°C, 1121°C, and 354°C respectively and are taken advantage of to make use of these elements in industry. In addition, elements in the iron triad are commonly combined with carbon and each other to create various types of alloys. It is because of these magnetic properties and use in alloys that the three elements are typically grouped together and labeled as the "Iron Triad". While very similar in magnetic properties and reaction, these elements are also very unique and used differently in both nature and industry.

Iron

Iron (Fe) is a transition metal with an atomic weight of 55.845 and an atomic number of 26. Its most common and comfortable oxidation state is +3 and is usually a shiny silver color. While it can be found in the sun and the stars, it is extremely common on planet earth and its abundance in the earth's crust is 4.7%. The pure metal form of iron is rarely found due to its ability to easily react with other metals and environments.

Iron's most common use in worldwide industry is to be used in alloys and steels for everyday use, some which even contain other elements in the Triad. By combining metals like iron with carbon to make alloys, very strong materials can be made that are used for steel housings, supports in television tubes, and other important products. Pure iron is available commercially in the United States and production of about 500 million tons of Iron is created every year throughout the world.

From a biological perspective, iron is essential to organisms since it's needed for the creation of hemoglobin. Humans need hemoglobin since these red pigments supply oxygen to our body through red blood cells. To increase intake of iron, foods like eggs, groundnuts and green leafy vegetables should be consumed. Without iron, our bodies would not be able to form hemoglobin and an organism would fail to survive.

Cobalt

Cobalt (Co) is a transition metal with an atomic weight of 58.93 and an atomic number of 27, right in between iron and nickel. Cobalt, however, is not as abundant as iron and only makes up of about 0.0020% of the Earth's crust. This makes cobalt a little more rare and valuable than the other members of the triad because it is still used heavily in international industry. It is for this reason that this hard gray element is mined for and traded around the world.

Like iron, this element is commonly combined with other metals to create alloys. Superalloys that contain cobalt are used for parts of gas turbine engines that benefit both commercial and military devices. In current times, however, the rise of rechargeable batteries has made demand for the element rise to new heights since it is commonly used for electrodes in this relatively new technology. While these are its most popular applications, cobalt is also utilized in the production of petroleum, dyes, magnets, and electronics due to its ferromagnetic properties.

Cobalt and its alloys have recently made strides in the biomedical sphere by playing a large role in neurological, dental, orthopedic, and cardiovascular implant devices. This is due to the fact that the alloys function well with their corrosion resistance, mechanical properties, and biocompatibility.

Nickel

Nickel (Ni), a transition metal with an atomic weight of 58.69 and an atomic number of 28, is usually recognized by its silvery shine with a hint of gold color. It was first discovered by Axel Fredrik Cronstedt in 1751 and named nickel from the ore "kupfernickel". Although nickel is not extremely common, it still ranks as #24 on the list of the most abundant elements on earth.

This element is most abundant in Canada and about 300 million pounds are used in America every year. Nickel is most commonly used as a key ingredient in low alloy steels, stainless steels, and cast irons. In fact, four out of five of these 300 million pounds of Nickel go to this type of alloy making. Like cobalt, it shares the unique characteristic of corrosion resistance and is ideal for corrosion and heat resistant coatings, magnetic alloys, and controlled-expansion alloys.



Over 2000 years ago, the Bactrian civilization in Western Asia used a 75:25 alloy of copper and nickel for its coins. A modern US nickel has the same composition, but a modern Canadian nickel is nickel-plated steel and contains only 2.5% nickel by mass.

New nickel-cadmium rechargeable batteries have also brought the use of nickel into a new light. Like cobalt, the turning of the millennium and the increased use of rechargeable batteries has given nickel a new major use that will likely surpass others in the future. Nickel-cadmium batteries have improved the performance of cordless power tools, portable computers, and other portable electronic devices.

Table 23.5.1: Chemical and Physical Properties of Iron Triad Elements

	Iron	**Cobalt**	**Nickel**
Atomic Number	26	27	28
Mass	55.85	58.93	58.69
Electron Configuration	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^1$
Metallic radius, pm	124	125	125

Ionization Energy, kJ mol^{-1}	762.5	760.4	737.1
• First	759	758	737
• Second	1561	1646	1753
• Third	2957	3232	3393
E°, V[b]	-0.440	-0.277	-0.257
Common (+) Oxidation States	2, 3, 6	2, 3	2, 3
Melting Point (°C)	1530	1495	1455
Boiling Point (°C)	2862	2927	2732
Density, g cm^{-3}	7.87	8.90	8.91
Electrical Conductivity[e]	16	25	23

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23.6: Group 11: Copper, Silver, and Gold

The coinage metals—copper, silver, and gold—occur naturally (like the gold nugget shown here); consequently, these were probably the first metals used by ancient humans. For example, decorative gold artifacts dating from the late Stone Age are known, and some gold Egyptian coins are more than 5000 yr old. Copper is almost as ancient, with objects dating to about 5000 BC. Bronze, an alloy of copper and tin that is harder than either of its constituent metals, was used before 3000 BC, giving rise to the Bronze Age. Deposits of silver are much less common than deposits of gold or copper, yet by 3000 BC, methods had been developed for recovering silver from its ores, which allowed silver coins to be widely used in ancient times.

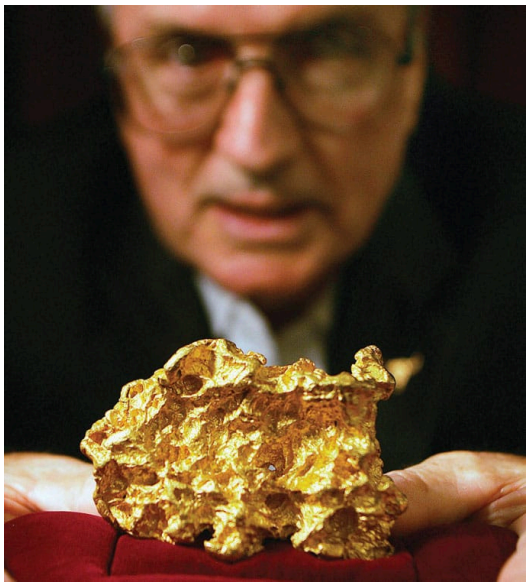


Figure 23.6.1: This 1 kg gold nugget was found in Australia; in 2005, it was for sale in Hong Kong at an asking price of more than US$64,000.

Deposits of gold and copper are widespread and numerous, and for many centuries it was relatively easy to obtain large amounts of the pure elements. For example, a single gold nugget discovered in Australia in 1869 weighed more than 150 lb. Because the demand for these elements has outstripped their availability, methods have been developed to recover them economically from even very low-grade ores (as low as 1% Cu content for copper) by operating on a vast scale, as shown in the photo of an open-pit copper mine. Copper is used primarily to manufacture electric wires, but large quantities are also used to produce bronze, brass, and alloys for coins. Much of the silver made today is obtained as a by-product of the manufacture of other metals, especially Cu, Pb, and Zn. In addition to its use in jewelry and silverware, silver is used in Ag/Zn and Ag/Cd button batteries. Gold is typically found either as tiny particles of the pure metal or as gold telluride ($AuTe_2$). It is used as a currency reserve, in jewelry, in the electronics industry for corrosion-free contacts, and, in very thin layers, as a reflective window coating that minimizes heat transfer.



Figure 23.6.2: The Chuquicamata copper mine in northern Chile, the world's largest open-pit copper mine, is 4.3 km long, 3 km wide, and 825 m deep. Each gigantic truck in the foreground (and barely visible in the lower right center) can hold 330 metric tn (330,000 kg) of copper ore.

Some properties of the coinage metals are listed in Table 23.6.1. The electronegativity of gold (χ = 2.40) is close to that of the nonmetals sulfur and iodine, which suggests that the chemistry of gold should be somewhat unusual for a metal. The coinage metals have the highest electrical and thermal conductivities of all the metals, and they are also the most ductile and malleable. With an $ns^1(n-1)d^{10}$ valence electron configuration, the chemistry of these three elements is dominated by the +1 oxidation state due to losing the single ns electron. Higher oxidation states are also known, however: +2 is common for Cu and, to a lesser extent, Ag, and +3 for Au because of the relatively low values of the second and (for Au) third ionization energies. All three elements have significant electron affinities due to the half-filled ns orbital in the neutral atoms. As a result, gold reacts with powerful reductants like Cs and solutions of the alkali metals in liquid ammonia to produce the gold anion Au^- with a $6s^25d^{10}$ valence electron configuration.

Table 23.6.1: Some Properties of the Elements of Groups 11

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
11	Cu	29	$4s^13d^{10}$	1.90	128	1085	8.96
	Ag	47	$5s^14d^{10}$	1.93	144	962	10.50
	Au	79	$6s^15d^{10}4f^{14}$	2.40	144	1064	19.30

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23.7: Group 12: Zinc, Cadmium, and Mercury

We next encounter the group 12 elements. Because none of the elements in group 12 has a partially filled (n – 1)d subshell, they are not, strictly speaking, transition metals. Nonetheless, much of their chemistry is similar to that of the elements that immediately precede them in the d block. The group 12 metals are similar in abundance to those of group 11, and they are almost always found in combination with sulfur. Because zinc and cadmium are chemically similar, virtually all zinc ores contain significant amounts of cadmium. All three metals are commercially important, although the use of Cd is restricted because of its toxicity. Zinc is used for corrosion protection, in batteries, to make brass, and, in the form of ZnO, in the production of rubber and paints. Cadmium is used as the cathode in rechargeable NiCad batteries. Large amounts of mercury are used in the production of chlorine and NaOH by the chloralkali process, while smaller amounts are consumed in mercury-vapor streetlights and mercury batteries.

As shown in Table 23.7.4, the group 12 metals are significantly more electropositive than the elements of group 11, and they therefore have less noble character. They also have much lower melting and boiling points than the preceding transition metals. In contrast to trends in the preceding groups, Zn and Cd are similar to each other, but very different from the heaviest element (Hg). In particular, Zn and Cd are rather active metals, whereas mercury is not. Because mercury, the only metal that is a liquid at room temperature, can dissolve many metals by forming amalgams, medieval alchemists especially valued it when trying to transmute base metals to gold and silver. All three elements in group 12 have $ns^2(n-1)d^{10}$ valence electron configurations; consequently, the +2 oxidation state, corresponding to losing the two ns electrons, dominates their chemistry. In addition, mercury forms a series of compounds in the +1 oxidation state that contain the diatomic mercurous ion Hg_2^{2+}.

Note

The most important oxidation state for group 12 is +2; the metals are significantly more electropositive than the group 11 elements, so they are less noble.

All the possible group 12 dihalides (MX_2) are known, and they range from ionic (the fluorides) to highly covalent (such as $HgCl_2$). The highly covalent character of many mercuric and mercurous halides is surprising given the large size of the cations, and this has been attributed to the existence of an easily distorted $5d^{10}$ subshell. Zinc and cadmium react with oxygen to form amphoteric MO, whereas mercury forms HgO only within a narrow temperature range (350–400°C). Whereas zinc and cadmium dissolve in mineral acids such as HCl with the evolution of hydrogen, mercury dissolves only in oxidizing acids such as HNO_3 and H_2SO_4. All three metals react with sulfur and the other chalcogens to form the binary chalcogenides; mercury also has an extraordinarily high affinity for sulfur.

Summary

The group 12 elements, whose chemistry is dominated by the +2 oxidation state, are almost always found in nature combined with sulfur. Mercury is the only metal that is a liquid at room temperature, and it dissolves many metals to form amalgams. The group 12 halides range from ionic to covalent. These elements form chalcogenides and have a high affinity for soft ligands.

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23.8: Lanthanides

The Lanthanides consist of the elements in the f-block of period six in the periodic table. While these metals can be considered transition metals, they have properties that set them apart from the rest of the elements.

Introduction

Lanthanides (elements 57–71) are fairly abundant in the earth's crust, despite their historic characterization as rare earth elements. Thulium, the rarest naturally occurring lanthanoid, is more common in the earth's crust than silver (4.5×10^{-5}% versus 0.79×10^{-5}% by mass). There are 17 rare earth elements, consisting of the 15 lanthanoids plus scandium and yttrium. They are called rare because they were once difficult to extract economically, so it was rare to have a pure sample; due to similar chemical properties, it is difficult to separate any one lanthanide from the others. However, newer separation methods, such as ion exchange resins similar to those found in home water softeners, make the separation of these elements easier and more economical. Most ores that contain these elements have low concentrations of all the rare earth elements mixed together.

Like any other series in the periodic table, such as the Alkali metals or the Halogens, the Lanthanides share many similar characteristics. These characteristics include the following:

- Similarity in physical properties throughout the series
- Adoption mainly of the +3 oxidation state. Usually found in crystalline compounds)
- They can also have an oxidation state of +2 or +4, though some lanthanides are most stable in the +3 oxidation state.
- Adoption of coordination numbers greater than 6 (usually 8-9) in compounds
- Tendency to decreasing coordination number across the series
- A preference for more electronegative elements (such as O or F) binding
- Very small crystal-field effects
- Little dependence on ligands
- Ionic complexes undergo rapid ligand-exchange

The commercial applications of lanthanides are growing rapidly. For example, europium is important in flat screen displays found in computer monitors, cell phones, and televisions. Neodymium is useful in laptop hard drives and in the processes that convert crude oil into gasoline (Figure 23.8.1). Holmium is found in dental and medical equipment. In addition, many alternative energy technologies rely heavily on lanthanoids. Neodymium and dysprosium are key components of hybrid vehicle engines and the magnets used in wind turbines.

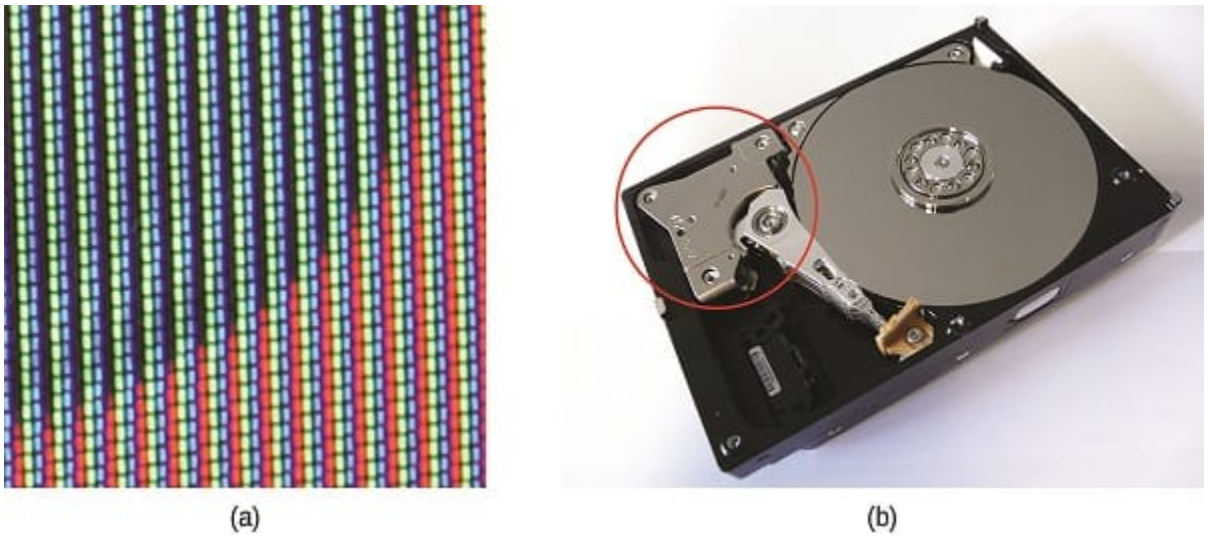


Figure 23.8.1: (a) Europium is used in display screens for televisions, computer monitors, and cell phones. (b) Neodymium magnets are commonly found in computer hard drives. (credit b: modification of work by "KUERT Datenrettung"/Flickr)

As the demand for lanthanide materials has increased faster than supply, prices have also increased. In 2008, dysprosium cost $110/kg; by 2014, the price had increased to $470/kg. Increasing the supply of lanthanoid elements is one of the most significant challenges facing the industries that rely on the optical and magnetic properties of these materials.

The transition elements have many properties in common with other metals. They are almost all hard, high-melting solids that conduct heat and electricity well. They readily form alloys and lose electrons to form stable cations. In addition, transition metals form a wide variety of stable coordination compounds, in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons. Many different molecules and ions can donate lone pairs to the metal center, serving as Lewis bases. In this chapter, we shall focus primarily on the chemical behavior of the elements of the first transition series.

Electron Configuration

Similarly, the Lanthanides have similarities in their electron configuration, which explains most of the physical similarities. These elements are different from the main group elements in the fact that they have electrons in the f orbital. After Lanthanum, the energy of the 4f sub-shell falls below that of the 5d sub-shell. This means that the electron start to fill the 4f sub-shell before the 5d sub-shell.

The electron configurations of these elements were primarily established through experiments (Table 23.8.1). The technique used is based on the fact that each line in an emission spectrum reveals the energy change involved in the transition of an electron from one energy level to another. However, the problem with this technique with respect to the Lanthanide elements is the fact that the 4f and 5d sub-shells have very similar energy levels, which can make it hard to tell the difference between the two.

Table 23.8.1: Electron Configurations of the Lanthanide Elements

Symbol	Idealized	Observed	Symbol	Idealized	Observed
La	$5d^16s^2$	$5d^16s^2$	Tb	$4f^85d^16s^2$	$4f^9\ 6s^2$ or $4f^85d^16s^2$
Ce	$4f^15d^16s^2$	$4f^15d^16s^2$	Dy	$4f^95d^16s^2$	$4f^{10}\ 6s^2$
Pr	$4f^25d^16s^2$	$4f^3\ 6s^2$	Ho	$4f^{10}5d^16s^2$	$4f^{11}\ 6s^2$
Nd	$4f^35d^16s^2$	$4f^4\ 6s^2$	Er	$4f^{11}5d^16s^2$	$4f^{12}\ 6s^2$
Pm	$4f^45d^16s^2$	$4f^5\ 6s^2$	Tm	$4f^{12}5d^16s^2$	$4f^{13}\ 6s^2$
Sm	$4f^55d^16s^2$	$4f^6\ 6s^2$	Yb	$4f^{13}5d^16s^2$	$4f^{14}\ 6s^2$
Eu	$4f^65d^16s^2$	$4f^7\ 6s^2$	Lu	$4f^{14}5d^16s^2$	$4f^{14}5d^16s^2$
Gd	$4f^75d^16s^2$	$4f^75d^16s^2$			

Another important feature of the Lanthanides is the Lanthanide Contraction, in which the 5s and 5p orbitals penetrate the 4f sub-shell. This means that the 4f orbital is not shielded from the increasing nuclear change, which causes the atomic radius of the atom to decrease that continues throughout the series.

Properties and Chemical Reactions

One property of the Lanthanides that affect how they will react with other elements is called the basicity. Basicity is a measure of the ease at which an atom will lose electrons. In another words, it would be the lack of attraction that a cation has for electrons or anions. For the Lanthanides, the basicity series is the following:

$$La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+}$$

In other words, the basicity decreases as the atomic number increases. Basicity differences are shown in the solubility of the salts and the formation of the complex species. Another property of the Lanthanides is their magnetic characteristics. The major magnetic properties of any chemical species are a result of the fact that each moving electron is a micromagnet. The species are either diamagnetic, meaning they have no unpaired electrons, or paramagnetic, meaning that they do have some unpaired electrons. The diamagnetic ions are: La^{3+}, Lu^{3+}, Yb^{2+} and Ce^{4+}. The rest of the elements are paramagnetic.

Table 23.8.2: Properties of the Lathanides

Symbol	Ionization Energy (kJ/mol)	Melting Point (°C)	Boiling Point (°C)
La	538	920	3469
Ce	527	795	3468
Pr	523	935	3127
Nd	529	1024	3027
Pm	536		
Sm	543	1072	1900
Eu	546	826	1429
Gd	593	1312	3000
Tb	564	1356	2800
Dy	572	1407	2600
Ho	581	1461	2600
Er	589	1497	2900
Tm	597	1545	1727
Yb	603	824	1427
Lu	523	1652	3327

Metals and their Alloys

The metals have a silvery shine when freshly cut. However, they can tarnish quickly in air, especially Ce, La and Eu. These elements react with water slowly in cold, though that reaction can happen quickly when heated. This is due to their electropositive nature. The Lanthanides have the following reactions:

- oxidize rapidly in moist air
- dissolve quickly in acids
- reaction with oxygen is slow at room temperature, but they can ignite around 150-200 °C
- react with halogens upon heating
- upon heating, react with S, H, C and N

Periodic Trends: Size

The size of the atomic and ionic radii is determined by both the nuclear charge and by the number of electrons that are in the electronic shells. Within those shells, the degree of occupancy will also affect the size. In the Lanthanides, there is a decrease in atomic size from La to Lu. This decrease is known as the Lanthanide Contraction. The trend for the entire periodic table states that the atomic radius decreases as you travel from left to right. Therefore, the Lanthanides share this trend with the rest of the elements.

Table 23.8.3: Periodic Trends

Element	Atomic Radius (pm)	Ionic Radius (3+)	Element	Atomic Radius (pm)	Ionic Radius (3+)
La	187.7	106.1	Tb	178.2	92.3
Ce	182	103.4	Dy	177.3	90.8
Pr	182.8	101.3	Ho	176.6	89.4

Nd	182.1	99.5	Er	175.7	88.1
Pm	181	97.9	Tm	174.6	89.4
Sm	180.2	96.4	Yb	194.0	85.8
Eu	204.2	95.0	Lu	173.4	84.8
Gd	180.2	93.8			

Color and Light Absorbance

The color that a substance appears is the color that is reflected by the substance. This means that if a substance appears green, the green light is being reflected. The wavelength of the light determines if the light with be reflected or absorbed. Similarly, the splitting of the orbitals can affect the wavelength that can be absorbed (Table 23.8.4). This is turn would be affected by the amount of unpaired electrons.

Table 23.8.4: : Unpaired Electrons and Color

Ion	Unpaired Electrons	Color	Ion	Unpaired Electrons	Color
La^{3+}	0	Colorless	Tb^{3+}	6	Pale Pink
Ce^{3+}	1	Colorless	Dy^{3+}	5	Yellow
Pr^{3+}	2	Green	Ho^{3+}	4	Pink; yellow
Nd^{3+}	3	Reddish	Er^{3+}	3	Reddish
Pm^{3+}	4	Pink; yellow	Tm^{3+}	2	Green
Sm^{3+}	5	Yellow	Yb^{3+}	1	Colorless
Eu^{3+}	6	Pale Pink	Lu^{3+}	0	Colorless
Gd^{3+}	7	Colorless			

Occurrence in Nature

Each known Lanthanide mineral contains all the members of the series. However, each mineral contains different concentrations of the individual Lanthanides. The three main mineral sources are the following:

- Monazite: contains mostly the lighter Lanthanides. The commercial mining of monazite sands in the United States is centered in Florida and the Carolinas
- Xenotime: contains mostly the heavier Lanthanides
- Euxenite: contains a fairly even distribution of the Lanthanides

In all the ores, the atoms with a even atomic number are more abundant. This allows for more nuclear stability, as explained in the Oddo-Harkins rule. The Oddo-Harkins rule simply states that the abundance of elements with an even atomic number is greater than the abundance of elements with an odd atomic number. In order to obtain these elements, the minerals must go through a separating process, known as separation chemistry. This can be done with selective reduction or oxidation. Another possibility is an ion-exchange method.

Note: The Oddo-Harkins Rule

The abundance of elements with an even atomic number is **greater** than the abundance of elements with an odd atomic number.

Applications

The pure metals of the Lanthanides have little use. However, the alloys of the metals can be very useful. For example, the alloys of Cerium have been used for metallurgical applications due to their strong reducing abilities. The Lanthanides can also be used for ceramic purposes. The almost glass-like covering of a ceramic dish can be created with the lanthanides. They are also used to improve the intensity and color balance of arc lights.

Like the Actinides, the Lanthanides can be used for nuclear purposes. The hydrides can be used as hydrogen-moderator carriers. The oxides can be used as diluents in nuclear fields. The metals are good for being used as structural components. The can also be used for structural-alloy-modifying components of reactors. It is also possible for some elements, such as Tm, to be used as portable x-ray sources. Other elements, such as Eu, can be used as radiation sources.

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23.9: High Temperature Superconductors

Learning Objectives

- To become familiar with the properties of superconductors.

Contributors

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23.E: Exercises

23.1: General Properties

23.2: Principles of Extractive Metallurgy

23.3: Metallurgy of Iron and Steel

23.4: First-Row Transition Metal Elements: Scandium to Manganese

Conceptual Problems

1. The valence electron configuration of Sc is $4s^2 3d^1$, yet it does not lose the d^1 electron to form 1+ ion. Why?
2. Give the ground-state electron configuration for Mn, Mn^{2+}, Au, Au^{3+}, Mo, and Mo^{5+}.
3. A great deal of research is being conducted on the use of titanium alloys as materials for transportation applications (airplanes, ships, automobiles, etc.). Why is Ti particularly suited to this purpose? What is the primary disadvantage that needs to be overcome?
4. Both Ti and Ta are used for bioimplants because they are highly resistant to corrosion. Their uses also extend to other applications where corrosion must be avoided. Why are these metals so corrosion resistant?
5. Give two reasons why Zr is used to make the casing for UO_2 fuel in water-cooled nuclear reactors.
6. Why is chromium added to steel to form stainless steel? What other elements might also be effective additives for this purpose? Why did you select these elements?
7. Tungsten is commonly used as the filament in electric light bulbs. Why is tungsten particularly suited to this purpose?
8. Palladium metal is used to purify H_2 by removing other gases. Why is Pd so permeable to H_2?
9. Give the valence electron configuration for Sc, Fe, Re, Ag, Zr, Co, V, Pr, Hg, Cr, Ni, Ce, Cu, and Tb.
10. The Hg–Hg bond is much stronger than the Cd–Cd bond, reversing the trend found among the other transition-metal groups. Explain this anomaly.
11. Which of the transition metals are most likely to form compounds in the +6 oxidation state? Why?

Structure and Reactivity

1. Do you expect $TiCl_4$, $TiCl_3$, $TiCl_2$, and Ti to be oxidized, reduced, or hydrolyzed by water? Explain your reasoning.
2. The atomic radii of vanadium, niobium, and tantalum are 134 pm, 146 pm, and 146 pm, respectively. Why does the radius increase from vanadium to niobium but not from niobium to tantalum?
3. The most stable oxidation state for the metals of groups 3, 4, and 5 is the highest oxidation state possible. In contrast, for nearly all the metals of groups 8, 9, and 10, intermediate oxidation states are most stable. Why?
4. Most of the transition metals can form compounds in multiple oxidation states. Ru, for example, can form compounds in the +8, +6, +4, +3, +2, and –2 oxidation states. Give the valence electron configuration of Ru in each oxidation state. Why does Ru exhibit so many oxidation states? Which ones are the most stable? Why?
5. Predict the maximum oxidation states of Cu, Cr, Mo, Rh, Zr, Y, Ir, Hg, and Fe.
6. In the +4 oxidation state all three group 7 metals form the dioxides (MO_2). Which of the three metals do you expect to form the most stable dioxide? Why?
7. Of $[Fe(H_2O)_6]^+$, $OsBr_7$, CoF_4, PtF_6, FeI_3, $[Ni(H_2O)_6]^{2+}$, OsO_4, IrO_4, NiO, RhS_2, and PtH, which do not exist? Why?
8. The chemistry of gold is somewhat anomalous for a metal. With which elements does it form the Au^- ion? Does it form a stable sulfide?
9. Of Os^{4+}, Pt^{10+}, Cr^{6+}, Ir^{9+}, Ru^{8+}, Re^{7+}, and Ni^{10+}, which are not likely to exist? Why?
10. Of Ag_2S, Cu_2S, AuI_3, CuF, AuF, AgN, and AuO, which are not likely to exist?
11. There is evidence that the Au^- ion exists. What would be its electron configuration? The compound CsAu has been isolated; it does not exhibit a metallic luster and does not conduct electricity. Is this compound an alloy? What type of bonding is

involved? Explain your answers.

12. Of Hg_2Cl_2, ZnO, HgF_2, $Cs_2[ZnCl_5]$, and HgNa, which are not likely to exist?
13. Mercurous oxide (Hg_2O) and mercurous hydroxide [$Hg_2(OH)_2$] have never been prepared. Why not? What products are formed if a solution of aqueous sodium hydroxide is added to an aqueous solution of mercurous nitrate [$Hg_2(NO_3)_2$]?
14. Arrange Fe_2O_3, TiO_2, V_2O_5, MoO_3, Mn_2O_7, and OsO_4 in order of increasing basicity.
15. Mercurous sulfide has never been prepared. What products are formed when H_2S gas is bubbled through an aqueous solution of mercurous nitrate?
16. Arrange Sc_2O_3, VO, V_2O_5, Cr_2O_3, Fe_2O_3, Fe_3O_4, and ZnO in order of increasing acidity.
17. Arrange Sc_2O_3, V_2O_5, CrO_3, Mn_2O_7, MnO_2, and VO_2 in order of increasing basicity.
18. Predict the products of each reaction and then balance each chemical equation.

    a. Ti + excess Cl_2, heated
    b. V_2O_5 in aqueous base
    c. $K_2Cr_2O_7 + H_2SO_4$
    d. $RuBr_2 + O_2$, in water
    e. $[CrO_4]^{2-}$ in aqueous acid
    f. Hg^{2+} + Hg, in aqueous acid

19. Predict the products of each reaction and then balance each chemical equation.
    a. AgBr + hν
    b. W + excess Cl_2, heated
    c. CuO + H_2, heated
    d. Fe_2O_3 in aqueous acid
    e. $RhCl_3 + NH_3$, in water
    f. Fe^{2+} + $[MnO_4]^-$, in water

20. What do you predict to be the coordination number of Pt^{2+}, Au^+, Fe^{3+}, and Os^{2+}?
21. Of La, Sc, Cr, and Hf, which is most likely to form stable compounds in the +4 oxidation state? Why?
22. Give the most common oxidation state for Y, W, Ru, Ag, Hg, Zn, Cr, Nb, and Ti.
23. Give the most common oxidation state for Os, Cd, Hf, V, Ac, Ni, Mn, Pt, and Fe.
24. Give the highest oxidation state observed for Zr, Fe, Re, Hg, Ni, La, and Mo.
25. Give the highest oxidation state observed for Ag, Co, Os, Au, W, and Mn.
26. Arrange La, Cs, Y, Pt, Cd, Mo, Fe, Co, and Ir in order of increasing first ionization energy.
27. Briefly explain the following trends within the transition metals.

    a. Transition-metal fluorides usually have higher oxidation states than their iodides.
    b. For a given metal, the lowest-oxidation-state oxide is basic and the highest-oxidation-state oxide is acidic.
    c. Halides of the transition metals become more covalent with increasing oxidation state and are more prone to hydrolysis.

28. Propose a method to prepare each of the following compounds: $TiCl_4[(CH_3)_2O]_2$, Na_2TiO_3, V_2O_5, and $Na_2Cr_2O_7$.
29. Of the group 5 elements, which

    a. has the greatest tendency to form ions in the lower oxidation states?
    b. has the greatest tendency to form a polymeric fluoride?
    c. does not form an MX_2 species?
    d. forms the most basic oxide?
    e. has the greatest tendency to form complexes with coordination numbers higher than 6?

Answers

9. Pt^{10+}, Ir^{9+}, and Ni^{10+}. Because ionization energies increase from left to right across the d block, by the time you reach group 9, it is impossible to form compounds in the oxidation state that corresponds to loss of all the valence electrons.

15. $Hg_2^{2+}(aq) + H_2S(g) \rightarrow Hg(l) + HgS(s) + 2H^+(aq)$

17. $Mn_2O_7 < CrO_3 < V_2O_5 < MnO_2 \approx VO_2 < Sc_2O_3$

19.

a. $2AgBr(s) \xrightarrow{light} 2Ag(s) + Br_2(l)$
b. $W(s) + \text{excess } Cl_2(g) \xrightarrow{\Delta} WCl_6(s)$
c. $CuO(s) + H_2(g) \xrightarrow{\Delta} Cu(s) + H_2O(g)$
d. $Fe_2O_3(s) + 6H^+(aq) \rightarrow 2Fe^{3+}(aq) + 3H_2O(l)$
e. $RhCl_3(s) + 6NH_3(aq) \rightarrow [Rh(NH_3)_6]Cl_3(aq)$
f. $3Fe^{2+}(aq) + MnO_4^-(aq) + 7H_2O(aq) \rightarrow Fe^{3+}(aq) + MnO_2(s) + 5H^+(l)$

23. Os, +4; Cd, +2; Hf, +4; V, +5; Ac, +3; Ni, +2; Mn, +2; Pt, +2 & +4; Fe, +2 & +3

25. Ag, +3; Co, +4; Os, +8; Au, +5; W, +6; Mn, +7

23.5: The Iron Triad: Iron, Cobalt, and Nickel

Practice Problems

1. $Fe_2O_3(s) + 3CO(g) \text{ --> } 2Fe\ (l) + 2CO_2(g)$

2. $5Fe^{2+}(aq) + MnO^{4-}(aq) + 8H^+(aq) \text{ --> } 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

3. $[Fe(H_2O)_6]^{3+} + SCN^-(aq) \text{ --> } [FeSCN(H_2O)_5]^{2+} + H_2O(l)$

4. $4FeS + 7O_2 \text{ --> } 2Fe_2O_3 + 4SO_2$

5. $Ni + H_2O$ --> No Reaction

23.6: Group 11: Copper, Silver, and Gold

23.7: Group 12: Zinc, Cadmium, and Mercury

23.8: Lanthanides

Practice Problems

1. Which elements are considered to be Lanthanides?
2. How do the Lanthanides react with oxygen?
3. What causes the Lanthanide Contraction?
4. Why do Lanthanides exhibit strong electromagnetic and light properties?
5. What do the Lanthanides have in common with the Noble Gases?

Answers

1. Elements Lanthanum (57) through Lutetium (71) on the periodic table are considered to be Lanthanides.
2. Lanthanides tend to react with oxygen to form oxides. The reaction at room temperature can be slow while heat can cause the reaction to happen rapidly.
3. The Lanthanide Contraction refers to the decrease in atomic size of the elements in which electrons fill the f-subshell. Since the f sub-shell is not shielded, the atomic size will decrease as the nuclear charge still increases.
4. Lanthanides exhibit strong electromagnetic and light properties because of the presence of unpaired electrons in the f-orbitals. The majority of the Lanthanides are paramagnetic, which means that they have strong magnetic fields.
5. Both the Lanthanides and Noble Gases tend to bind with more electronegative atoms, such as Oxygen or Fluorine.

23.9: High Temperature Superconductors

1. Why does the BCS theory predict that superconductivity is not possible at temperatures above approximately 30 K?
2. How does the formation of Cooper pairs lead to superconductivity?

Solution

1. According to BCS theory, the interactions that lead to formation of Cooper pairs of electrons are so weak that they should be disrupted by thermal vibrations of lattice atoms above about 30 K.

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24: COMPLEX IONS AND COORDINATION COMPOUNDS

Petrucci: *General Chemistry*
Principles and Modern Applications

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24.1: Werner's Theory of Coordination Compounds

Learning Objectives

- To know the most common structures observed for metal complexes.
- To predict the relative stabilities of metal complexes with different ligands

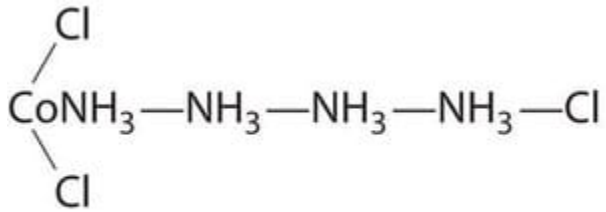
One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands (from the Latin ligare, meaning "to bind"), which are ions or molecules that contain one or more pairs of electrons that can be shared with the metal. Metal complexes can be neutral, such as $Co(NH_3)_3Cl_3$; positively charged, such as $[Nd(H_2O)_9]^{3+}$; or negatively charged, such as $[UF_8]^{4-}$. Electrically charged metal complexes are sometimes called *complex ions*. A *coordination compound* contains one or more metal complexes.

Coordination compounds are important for at least three reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene "plastic" items we use every day. Finally, transition-metal complexes are essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions.

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue: $KFe_2(CN)_6$. The chemical nature of these substances, however, was unclear for a number of reasons. For example, many compounds called "double salts" were known, such as $AlF_3 \cdot 3\,KF$, $Fe(CN)_2 \cdot 4\,KCN$, and $ZnCl_2 \cdot 2\,CsCl$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $AlF_3 \cdot 3\,KF$ exist but not $AlF_3 \cdot 4\,KF$ or $AlF_3 \cdot 2\,KF$? And why should a 3:1 KF:AlF3 mixture have different chemical and physical properties than either of its components? Similarly, adducts of metal salts with neutral molecules such as ammonia were also known—for example, $CoCl_3 \cdot 6\,NH_3$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $CoCl_3 \cdot 6\,NH_3$, $CoCl_3 \cdot 5\,NH_3$, $CoCl_3 \cdot 4\,NH_3$, and $CoCl_3 \cdot 3\,NH_3$ were all known and had very different properties, but despite all attempts, chemists could not prepare $CoCl_3 \cdot 2\,NH_3$ or $CoCl_3 \cdot NH_3$.

Although the chemical composition of such compounds was readily established by existing analytical methods, their chemical nature was puzzling and highly controversial. The major problem was that what we now call valence (i.e., the oxidation state) and coordination number were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds, including the "Chattanooga choo-choo" model for $CoCl_3$·4NH_3 shown here.



$CoCl_3 \cdot 4NH_3$

The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several

series of metal halide complexes with ammonia. For example, five different "adducts" of ammonia with $PtCl_4$ were known at the time: $PtCl_4{\cdot}nNH_3$ (n = 2–6). Some of Werner's original data on these compounds are shown in Table 24.1.1. The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding $Ag^+(aq)$ was a measure of the number of "free" chloride ions present. For example, Werner's data on $PtCl_4{\cdot}6NH_3$ in Table 24.1.1 showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4{\cdot}2NH_3$ was a neutral molecule that contained no free chloride ions.

Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table 24.1.1: Werner's Data on Complexes of Ammonia with $PtCl_4$

Complex	Conductivity (ohm^{-1})	Number of Ions per Formula Unit	Number of Cl^- Ions Precipitated by Ag^+
$PtCl_4{\cdot}6NH_3$	523	5	4
$PtCl_4{\cdot}5NH_3$	404	4	3
$PtCl_4{\cdot}4NH_3$	299	3	2
$PtCl_4{\cdot}3NH_3$	97	2	1
$PtCl_4{\cdot}2NH_3$	0	0	0

These data led Werner to postulate that metal ions have two different kinds of valence: (1) a primary valence (**oxidation state**) that corresponds to the positive charge on the metal ion and (2) a secondary valence (**coordination number**) that is the total number of ligand-metal bonds bound to the metal ion. If Pt had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $PtCl_4 \cdot NH_3$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

$$[Pt(NH_3)_6]Cl_4 \rightarrow [Pt(NH_3)_6]^{4+}(aq) + 4Cl^-(aq)$$
$$[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+}(aq) + 3Cl^-(aq)$$
$$[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+}(aq) + 2Cl^-(aq)$$
$$[Pt(NH_3)_3Cl_3]Cl \rightarrow [Pt(NH_3)_3Cl_3]^{+}(aq) + Cl^-(aq)$$
$$[Pt(NH_3)_2Cl_4] \rightarrow [Pt(NH_3)_2Cl_4]^{0}(aq)$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for Co^{3+} and Cr^{3+} and 4 for Pt^{2+} and Pd^{2+}.

Werner's studies on the analogous Co^{3+} complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (Figure 24.1.1*a*). Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (Figure 24.1.1*b*. His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.

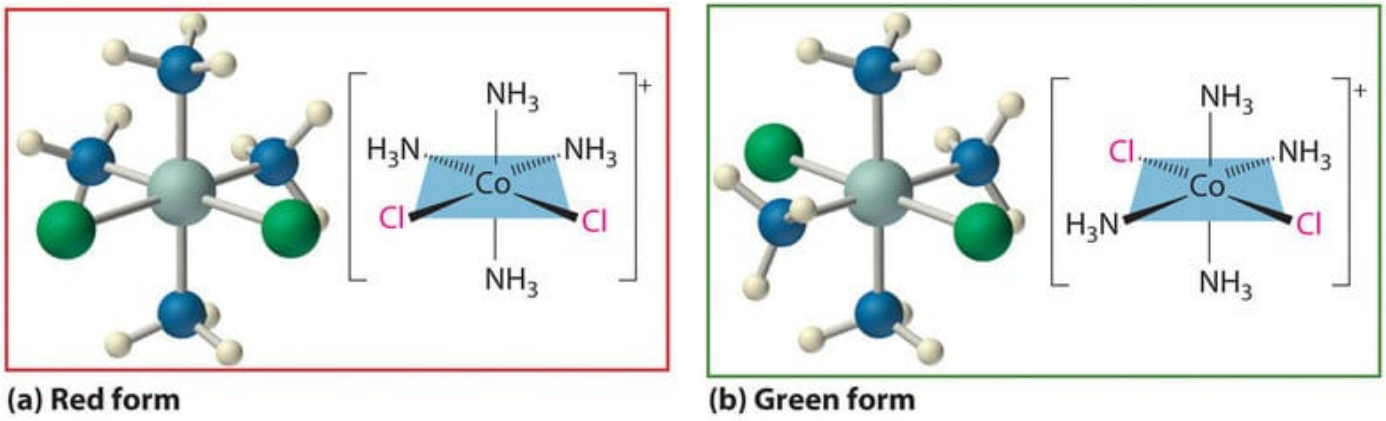


Figure 24.1.1: Complexes with Different Arrangements of the Same Ligands Have Different Properties. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).

Example 24.1.1

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning, calculate the maximum number of different structures that are possible for six-coordinate MA_4B_2 complexes with each of the three most symmetrical possible structures: a hexagon, a trigonal prism, and an octahedron. What does the fact that no more than two forms of any MA_4B_2 complex were known tell you about the three-dimensional structures of these complexes?

Given: three possible structures and the number of different forms known for MA_4B_2 complexes

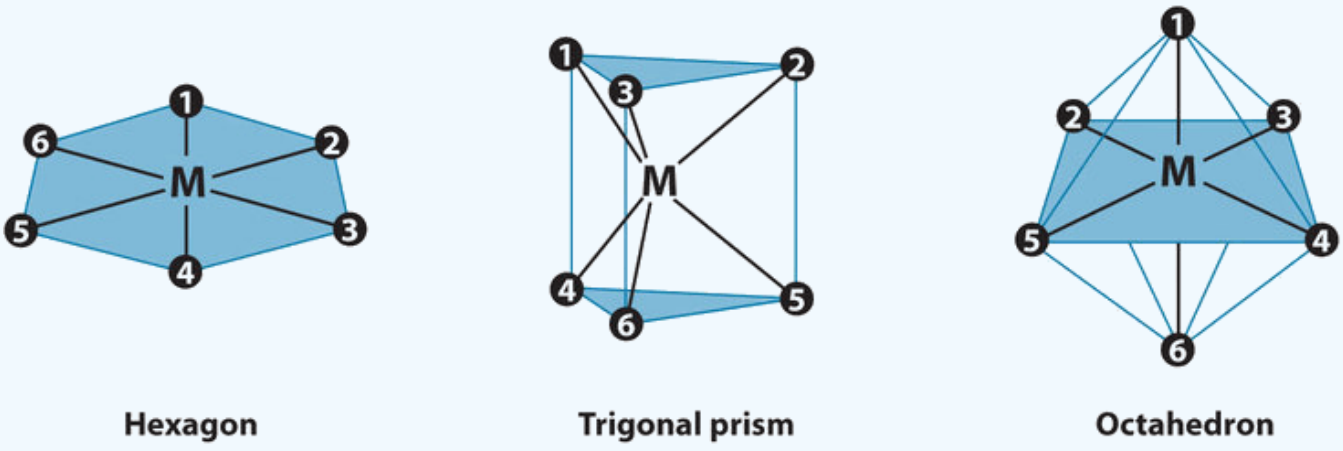
Asked for: number of different arrangements of ligands for MA_4B_2 complex for each structure

Strategy:

Sketch each structure, place a B ligand at one vertex, and see how many different positions are available for the second B ligand.

Solution

The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical MA_6 complex and simply replace two of the A ligands in each structure to give an MA_4B_2 complex:



For the hexagon, we place the first B ligand at position 1. There are now three possible places for the second B ligand: at position 2 (or 6), position 3 (or 5), or position 4. These are the only possible arrangements. The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand: at position 2 or 3 on the same triangular face, position 4 (on the other triangular face but adjacent to 1), or position 5 or 6 (on the other triangular face but not adjacent to 1). The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., MA_3B_3), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

Exercise 24.1.1

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer available at the end of this section.

Structures of Metal Complexes

The coordination numbers of metal ions in metal complexes can range from 2 to at least 9. In general, the differences in energy between different arrangements of ligands are greatest for complexes with low coordination numbers and decrease as the coordination number increases. Usually only one or two structures are possible for complexes with low coordination numbers, whereas several different energetically equivalent structures are possible for complexes with high coordination numbers ($n > 6$). The following presents the most commonly encountered structures for coordination numbers 2–9. Many of these structures should be familiar to you from our discussion of the valence-shell electron-pair repulsion (VSEPR) model because they correspond to the lowest-energy arrangements of n electron pairs around a central atom.

> Compounds with low coordination numbers exhibit the greatest differences in energy between different arrangements of ligands.

Coordination Number 2

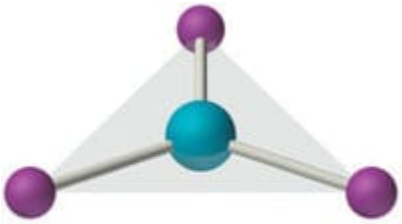
Although it is rare for most metals, this coordination number is surprisingly common for d^{10} metal ions, especially Cu^+, Ag^+, Au^+, and Hg^{2+}. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores. As expected based on VSEPR considerations, these complexes have the linear L–M–L structure shown here.



Linear ML_2

Coordination Number 3

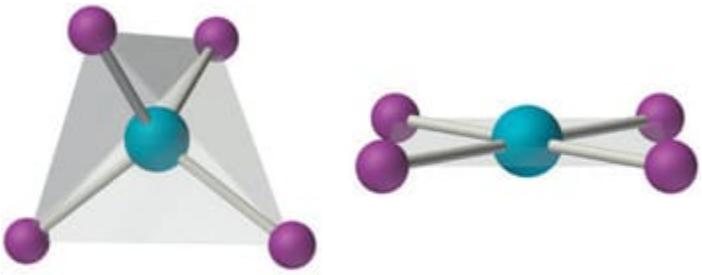
Although it is also rare, this coordination number is encountered with d^{10} metal ions such as Cu^{+} and Hg^{2+}. Among the few known examples is the HgI_3^{-} ion. Three-coordinate complexes almost always have the trigonal planar structure expected from the VSEPR model.



Trigonal planar ML_3

Coordination Number 4

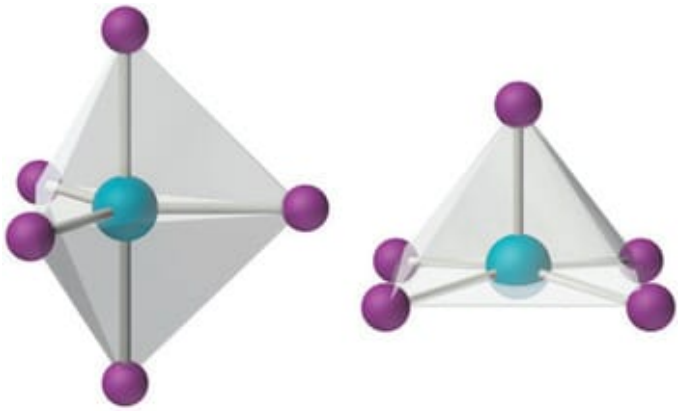
Two common structures are observed for four-coordinate metal complexes: tetrahedral and square planar. The tetrahedral structure is observed for all four-coordinate complexes of nontransition metals, such as $[BeF_4]^{2-}$, and d^{10} ions, such as $[ZnCl_4]^{2-}$. It is also found for four-coordinate complexes of the first-row transition metals, especially those with halide ligands (e.g., $[FeCl_4]^{-}$ and $[FeCl_4]^{2-}$). In contrast, square planar structures are routinely observed for four-coordinate complexes of second- and third-row transition metals with d^8 electron configurations, such as Rh^{+} and Pd^{2+}, and they are also encountered in some complexes of Ni^{2+} and Cu^{2+}.



Tetrahedral and square planar ML_4

Coordination Number 5

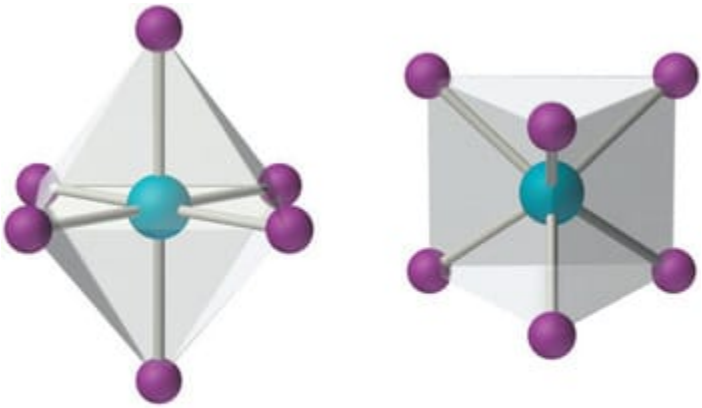
This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures that lie somewhere between the two extremes.



Trigonal bipyramidal and square pyramidal ML_5

Coordination Number 6

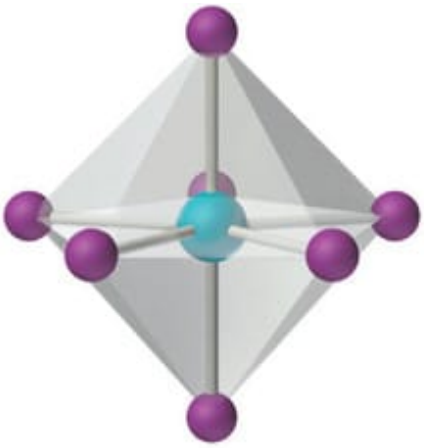
This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.



Octahedral and trigonal prismatic ML_6

Coordination Number 7

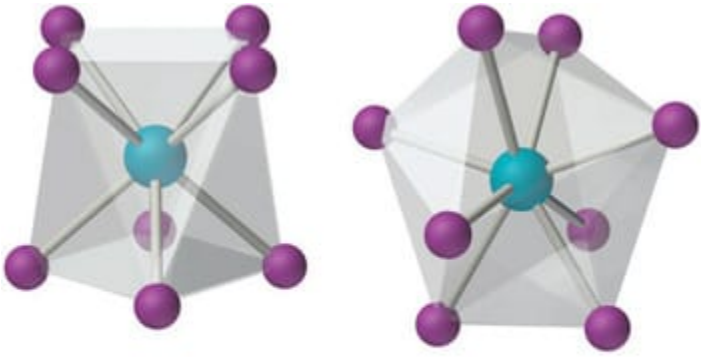
This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand to one face of the polyhedron to give a “capped” octahedron or trigonal prism. By far the most common, however, is the pentagonal bipyramid.



Pentagonal bipyramidal ML_7

Coordination Number 8

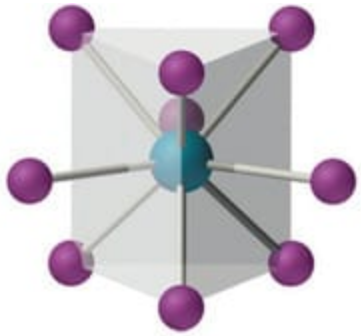
This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.



Square antiprismatic and trigonal dodecahedral ML_8

Coordination Number 9

This coordination number is found in larger metal ions, and the most common structure is the tricapped trigonal prism, as in $[Nd(H_2O)_9]^{3+}$.



Tricapped trigonal prismatic ML_9

Key Takeaways

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

Summary

Transition metals form metal complexes, polyatomic species in which a metal ion is bound to one or more ligands, which are groups bound to a metal ion. Complex ions are electrically charged metal complexes, and a coordination compound contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures. Coordination numbers of two and three are common for d^{10} metal ions. Tetrahedral and square planar complexes have a coordination number of four; trigonal bipyramidal and square pyramidal complexes have a coordination number of five; and octahedral complexes have a coordination number of six. At least three structures are known for a coordination number of seven, which is generally found for only large metal ions. Coordination numbers of eight and nine are also found for larger metal ions.

Answers

Exercise 24.1.1

square planar, 2; tetrahedral, 1

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24.2: Ligands

A metal ion in solution does not exist in isolation, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it. Ligands are ions or neutral molecules that bond to a central metal atom or ion. Ligands act as Lewis bases (electron pair donors), and the central atom acts as a Lewis acid (electron pair acceptor). Ligands have at least one donor atom with an electron pair used to form covalent bonds with the central atom.

The term ligand come from the latin word *ligare* (which meaning to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. Ligands can be anions, cations, or neutral molecules. Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced, hence the idea of bite angle etc. A monodentate ligand has only one donor atom used to bond to the central metal atom or ion.

Monodentate Ligands

The term "monodentate" can be translated as "one tooth," referring to the ligand binding to the center through only one atom. Some examples of monodentate ligands are: chloride ions (referred to as chloro when it is a ligand), water (referred to as aqua when it is a ligand), hydroxide ions (referred to as hydroxo when it is a ligand), and ammonia (referred to as ammine when it is a ligand).

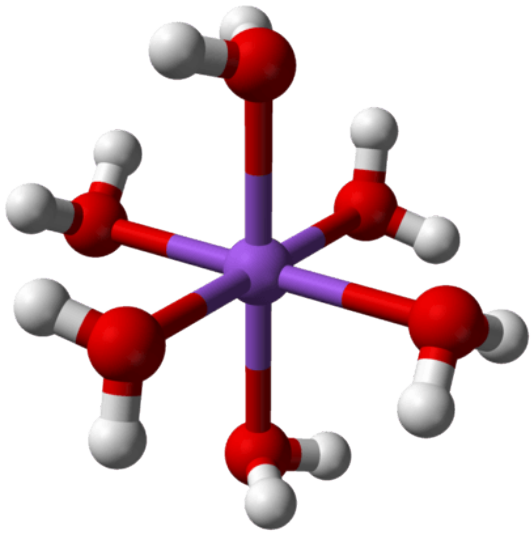


Figure 24.2.1: Central atom with six monodentate ligands attached. (Image courtesy of Wikimedia Commons.)

Bidentate Ligands

Bidentate ligands have two donor atoms which allow them to bind to a central metal atom or ion at two points. Common examples of bidentate ligands are ethylenediamine (en), and the oxalate ion (ox). Shown below is a diagram of ethylenediamine: the nitrogen (blue) atoms on the edges each have two free electrons that can be used to bond to a central metal atom or ion.

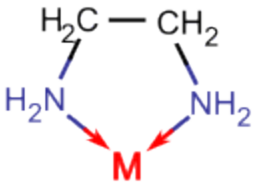


Figure 24.2.2: Ethylenediamine (en) is an example of a bidentate ligand. (Image courtesy of Wikimedia Commons.). Ethylenediamine (en) is a bidentate ligand that forms a five-membered ring in coordinating to a metal ion M

Polydentate Ligands

Polydentate ligands range in the number of atoms used to bond to a central metal atom or ion. EDTA, a hexadentate ligand, is an example of a polydentate ligand that has six donor atoms with electron pairs that can be used to bond to a central metal atom or ion.

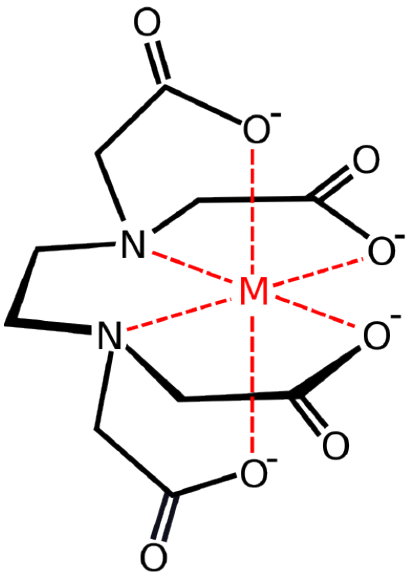
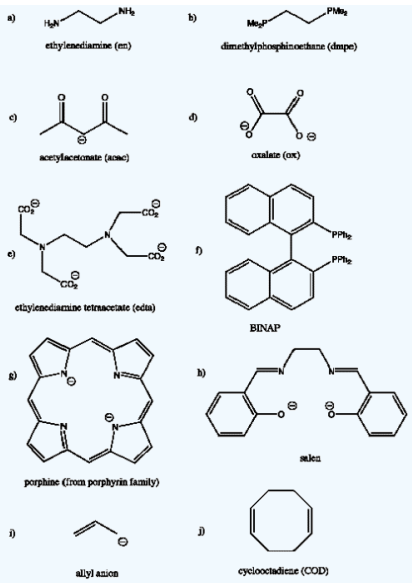


Figure 24.2.3: Ethylenediaminetetraaceticacid acid (EDTA) is a hexadentate ligand and can bind a Metal via multiple "teeth" (left) Unbound EDTA ion and (right) EDTA bound to a generic transition metal. (Images courtesy of Wikimedia Commons.)

Unlike polydentate ligands, ambidentate ligands can attach to the central atom in two places. A good example of this is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom.

Example 24.2.1

Draw metal complexes using the ligands below and metal ions of your choice.



Chelation

Chelation is a process in which a polydentate ligand bonds to a metal ion, forming a ring. The complex produced by this process is called a chelate, and the polydentate ligand is referred to as a chelating agent. The term chelate was first applied in 1920 by Sir Gilbert T. Morgan and H.D.K. Drew, who stated: "The adjective chelate, derived from the great claw or chela (chely- Greek) of the lobster or other crustaceans, is suggested for the caliperlike groups which function as two associating units and fasten to the central atom so as to produce heterocyclic rings." As the name implies, chelating ligands have high affinity for metal ions relative to ligands with only one binding group (which are called monodentate = "single tooth") ligands. Both Ethylenediamine (Figure 24.2.2) and Ethylenediaminetetraaceticacid acid (Figure 24.2.3) are examples of chelating agents, but many others are commonly found in the inorganic laboratory.

The Chelate Effect

The chelate effect is the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar nonchelating (monodentate) ligands for the same metal.

The **macrocyclic effect** follows the same principle as the chelate effect, but the effect is further enhanced by the cyclic conformation of the ligand. Macrocyclic ligands are not only multi-dentate, but because they are covalently constrained to their cyclic form, they allow less conformational freedom. The ligand is said to be "pre-organized" for binding, and there is little entropy penalty for wrapping it around the metal ion. For example heme b is a tetradentate cyclic ligand that strongly complexes transition metal ions, including Fe^{+2} in hemogloben (Figure 24.2.4).

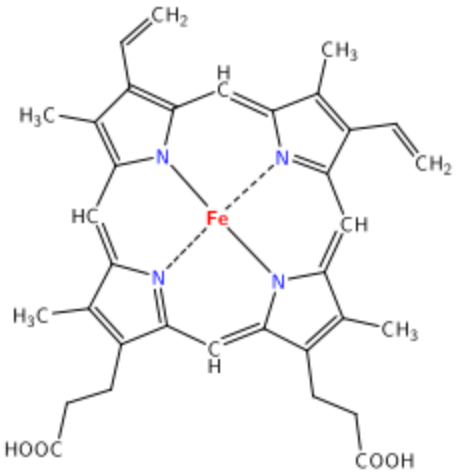
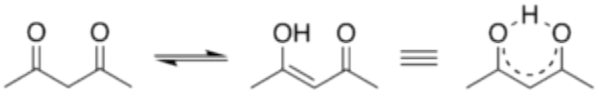


Figure 24.2.4: Heme b macrocyclic ligand that binds iron in hemoglobin

Some other common chelating and cyclic ligands are shown below:

- **Acetylacetonate** ($acac^-$, top) is an anionic bidentate ligand that coordinates metal ions through two oxygen atoms. $Acac^-$ is a hard base so it prefers hard acid cations. With divalent metal ions, $acac^-$forms neutral, volatile complexes such as $Cu(acac)_2$ and $Mo(acac)_2$ that are useful for chemical vapor deposition (CVD) of metal thin films.



- **2,2'-Bipyridine 2,2'-Bipyridine** (Figure 24.2.5: left) and related bidentate ligands such as 1,10-phenanthroline form propeller-shaped complexes with metals such as Ru^{2+}. The $[Ru(bpy)_3]^{2+}$ complex is photoluminescent and can also undergo photoredox reactions, making it an interesting compound for both photocatalysis and artificial photosynthesis.
- **Crown ethers** such as 18-crown-6 **2,2'-Bipyridine** (Figure 24.2.5: center) are cyclic hard bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.
- The chelating properties of crown ethers are mimetic of the natural antibiotic **valinomycin** (**2,2'-Bipyridine** (Figure 24.2.5 : right), which selectively transports K^+ ions across bacterial cell membranes, killing the bacterium by dissipating its membrane potential. Like crown ethers, valinomycin is a cyclic hard base.

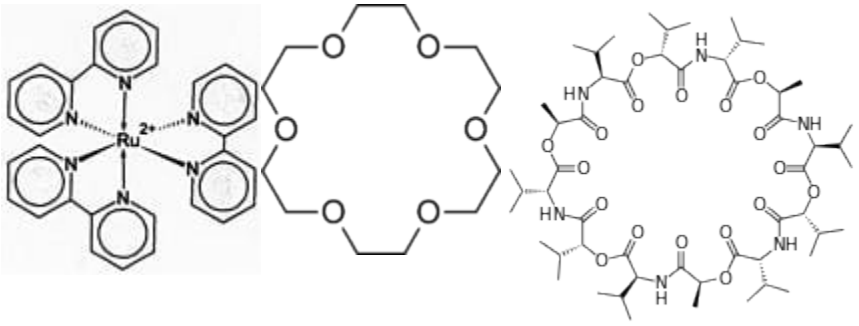


Figure 24.2.5: (let) 2,2'-Bipyridine, (center) 18-crown-6 2,2'-Bipyridine (right) valinomycin

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24.3: Complex Ion Nomenclature

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 24.3.1: 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 24.3.2: 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 24.3.3: 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 24.3.4: 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 24.3.1

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 24.3.1

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 24.3.5: 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 24.3.3). Here are some examples with determining oxidation states, naming a metal in an anion complex, and naming coordination compounds.

Example 24.3.2

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 24.3.2

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 24.3.3

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 24.3.3: 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 24.3.4

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 24.3.4

Write the chemical formulas for

a. Amminetetraaquachromium (II) sulfate
b. Potassium hexacyanoferrate (III)

Answer available at the end of this section.

Answers

Exercise 24.3.1

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 24.3.2

tetrachlorocuprate(II) ion

Exercise 24.3.3**: 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 24.3.4

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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24.4: Isomerism in Coordination Complexes

Learning Objectives

- Explain the differences of Structural and Geometric isomerization in a coordination complexes or complex ions.
- Define Ionization, Linkage, and Coordination Isomerization (structural isomer classes)
- Define cis/tran and mer/fac isomerization (geometric isomer classes)

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. 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. Isomers are compounds with the same molecular formula but different structural formulas and do not necessarily share similar properties. There are many different classes of isomers, like stereoisomers, enantiomers, and geometrical isomers. There are two main forms of isomerism: **structural isomerism** and **stereoisomerism** (spatial isomerism).

Class I: Structural Isomers

Isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another are called structural isomers, which differ in structure or bond type. For inorganic complexes, there are three types of structural isomers: *ionization*, *coordination* and *linkage*. Structural isomers, as their name implies, differ in their structure or bonding, which are separate from stereoisomers that differ in the spatial arrangement of the ligands are attached, but still have the bonding properties. The different chemical formulas in structural isomers are caused either by a difference in what ligands are bonded to the central atoms or how the individual ligands are bonded to the central atoms. When determining a structural isomer, you look at (1) the ligands that are bonded to the central metal and (2) which atom of the ligands attach to the central metal.

Ionization Isomerism

Ionization isomers occur when a ligand that is bound to the metal center exchanges places with an anion or neutral molecule that was originally outside the coordination complex. The geometry of the central metal ion and the identity of other ligands are identical. For example, an octahedral isomer will have five ligands that are identical, but the sixth will differ. The non-matching ligand in one compound will be outside of the coordination sphere of the other compound. Because the anion or molecule outside the coordination sphere is different, the chemical properties of these isomers is different. A hydrate isomer is a specific kind of ionization isomer where a water molecule is one of the molecules that exchanges places.

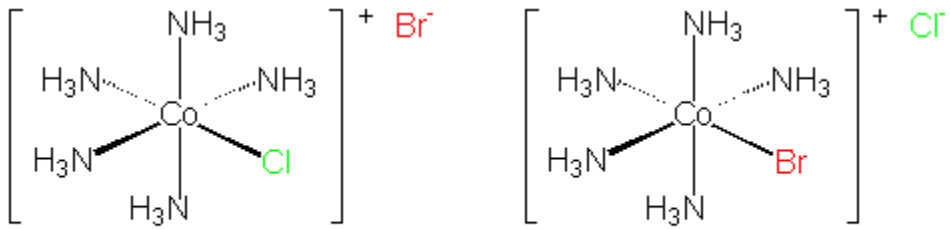


Figure 24.4.1: Ionization isomerism. The two isomers differ only in which ligands are bound to the center metal and which are counter ions in the second coordination sphere. (left) The chloride ion is bound to the cobalt as a chloro-ligand with the bromide ion as the counter ion. (right) In the other ionization isomer the bromide is acting as a bromo-ligand to the cobalt with the chloride acting as the counter ion. These two isomers are called pentaamminechlorocobalt(II) bromide (left) and pentaamminebromocobalt(II) chloride (right).

The difference between the ionization isomers can be view within the context of the ions generated when each are dissolved in solution. For example, when pentaamminebromocobalt(II) chloride is dissolved in water, Cl^- ions are generated:

$$\mathrm{CoBr(NH_3)_5Cl\ (s)\ \rightarrow CoBr(NH_3)_5^+\,(aq) + Cl^-\,(aq)} \tag{24.4.1}$$

whereas when pentaamminechlorocobalt(II) bromide is dissolved, $\mathrm{Br^-}$ ions are generated:

$$\mathrm{CoCl(NH_3)_5Br\ (s)\ \rightarrow CoCl(NH_3)_5^+\,(aq) + Br^-\,(aq)} \tag{24.4.2}$$

Notice that both anions are necessary to balance the charge of the complex, and that they differ in that one ion is directly attached to the central metal, but the other is not.

Solvate and Hydrate Isomerism: A special Type of Ionization Isomers

A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (*Solvate Isomerism*), which in the case of water is called *Hydrate Isomerism*. The best known example of this occurs for chromium chloride ($\mathrm{CrCl_3\ \cdot 6\,H_2O}$) which may contain 4, 5, or 6 coordinated water molecules (assuming a coordination number of 6). The dot here is used essentially as an expression of ignorance to indicate that, though the parts of the molecule separated by the dot are bonded to one another in some fashion, the exact structural details of that interaction are not fully expressed in the resulting formula. Alfred Werner's coordination theory indicates that several of the water molecules are actually bonded directly (via coordinate covalent bonds) to the central chromium ion. In fact, there are several possible compounds that use the brackets to signify bonding in the complex and the dots to signify "water molecules that are not bound to the central metal, but are part of the lattice:

- $\mathrm{[CrCl_2(H_2O)_4]Cl\ \cdot 2\,H_2O}$: bright-green colored
- $\mathrm{[CrCl(H_2O)_5]Cl_2\ \cdot H_2O}$: grey-green colored
- $\mathrm{[Cr(H_2O)_6]Cl_3}$: violet colored

These isomers have very different chemical properties and on reaction with $\mathrm{AgNO_3}$ to test for $\mathrm{Cl^-}$ ions, would find 1, 2, and 3 $\mathrm{Cl^-}$ ions in solution, respectively.

Upon crystallization from water, many compounds incorporate water molecules in their crystalline frameworks. These "waters of crystallization" refers to water that is found in the crystalline framework of a metal complex or a salt, which is **not directly bonded** to the metal cation. In the first two hydrate isomers, there are water molecules that are artifacts of the crystallization and occur inside crystals. These waters of crystallization contribute to the total weight of water in a substance and are mostly present in a definite (stoichiometric) ratio.

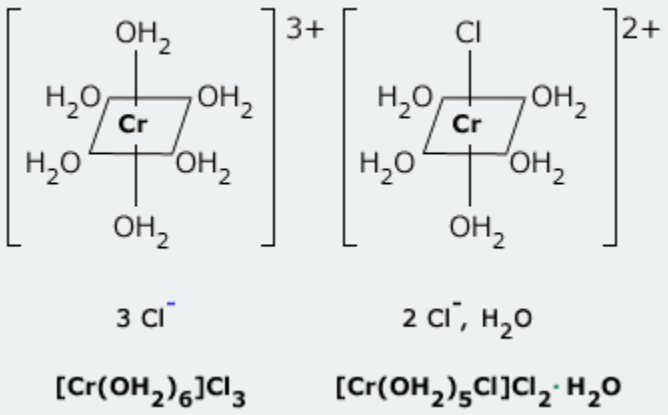


Figure 24.4.2: Hydrate iosomerisim. The $\mathrm{[Cr(H_2O)_6]Cl_3}$ hydrate isomer (left) is violet colored and the $\mathrm{[CrCl(H_2O)_5]Cl_2\ \cdot H_2O}$ hydrate isomer is green-grey colored.

What are "Waters of Crystallization"?

A compound with associated water of crystallization is known as a hydrate. The structure of hydrates can be quite elaborate, because of the existence of hydrogen bonds that define polymeric structures. For example, consider the aquo complex $NiCl_2 \cdot 6\,H_2O$ that consists of separated *trans*-[$NiCl_2(H_2O)_4$] molecules linked more weakly to adjacent water molecules. Only four of the six water molecules in the formula are bound to the nickel (II) cation, and the remaining two are waters of crystallization as the crystal structure resolves (Figure 24.4.3).

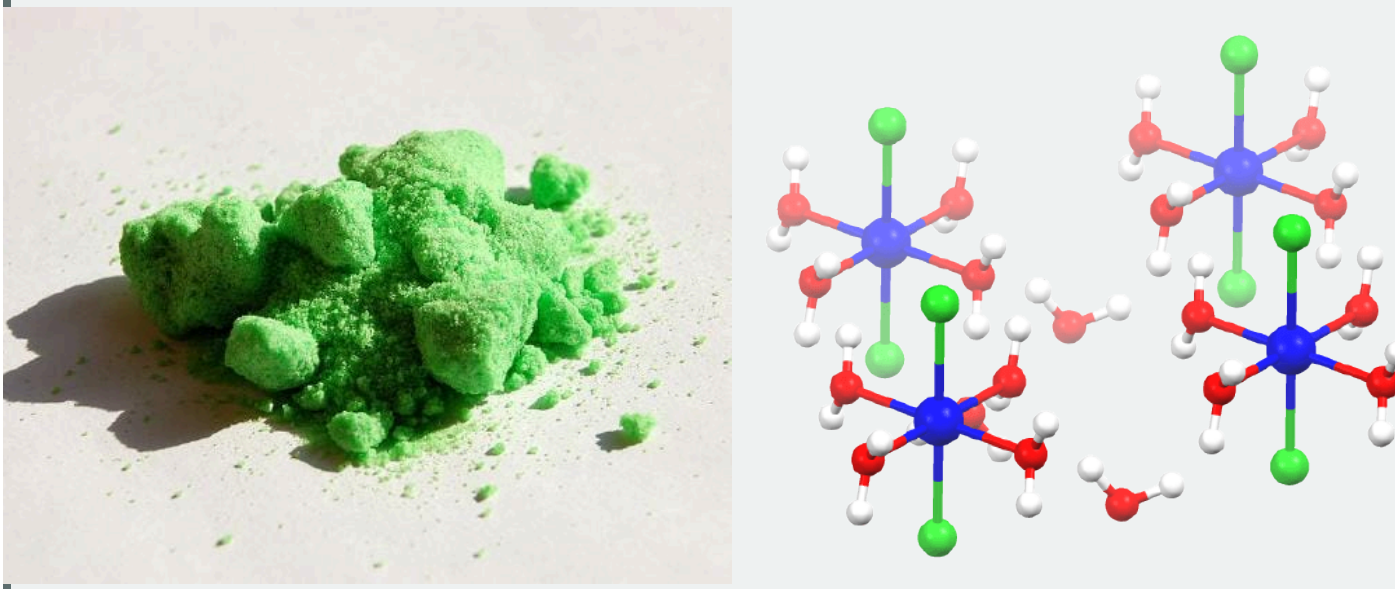


Figure 24.4.3: Water of hydration. (left) Image of $NiCl_2 \cdot 6\,H_2O$ salt (Public Domain; Benjah-bmm27 via Wikipedia). (right) Crystal Structure of $NiCl_2 \cdot 6\,H_2O$ with chlorine atoms (green), water molecules (red), and Ni metals (blue) indicated. Note that only four of the waters are bound as ligands to the nickel ions and two are outside of the coordination sphere. (CC BY-SA 4.0; Smokefoot).

Water is particularly common solvent to be found in crystals because it is small and polar. But *all* solvents can be found in some host crystals. Water is noteworthy because it is reactive, whereas other solvents such as benzene are considered to be chemically innocuous.

Coordination Isomerism

Coordination isomerism occurs in compounds containing complex anionic and complex cationic parts and can be viewed as an interchange of some ligands from the cation to the anion. Hence, there are two complex compounds bound together, one with a negative charge and the other with a positive charge. In coordination isomers, the anion and cation complexes of a coordination compound exchange one or more ligands. For example, the $[Zn(NH_3)_4]\,[Cu(Cl_4)]$ and $[Cu(NH_3)_4]\,[Zn(Cl_4)]$ compounds are coordination isomers (Figure 24.4.4).

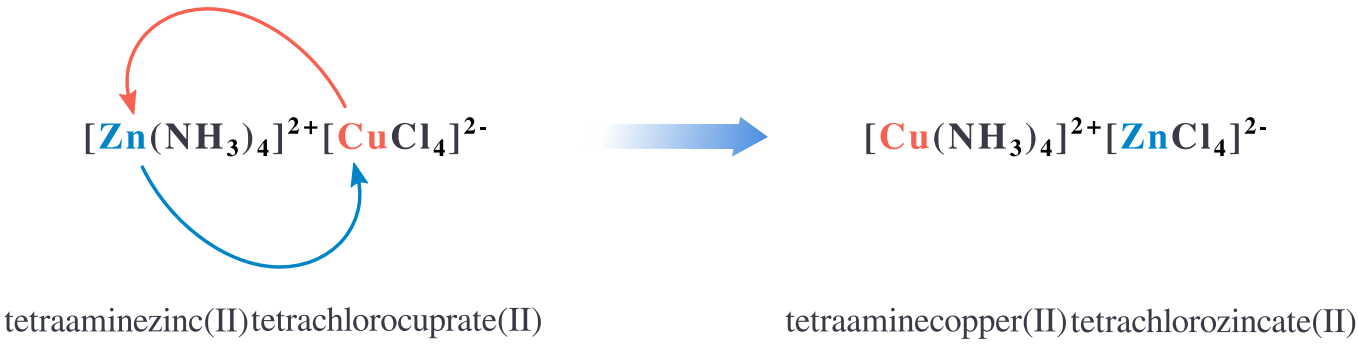


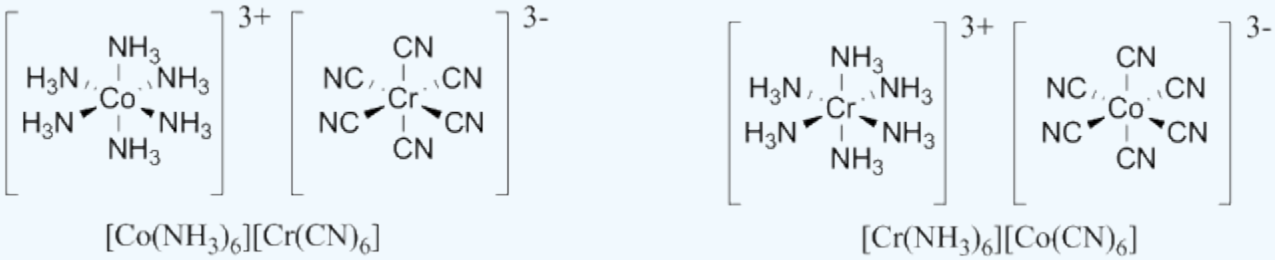
Figure 24.4.4: Coordination Isomerism. (CC BY-NC; Ümit Kaya)

Example 24.4.2: Coordination Isomers

What is the coordination isomer for the $[Co(NH_3)_6]\ [Cr(CN)_6]$ compound?

Solution

Coordination isomerism involves switching the metals between the cation and anion spheres.



Hence the $[Cr(NH_3)_6][Co(CN)_6]$ compound is a coordination isomer of $[Co(NH_3)_6]\ [Cr(CN)_6]$.

Linkage Isomerism

Linkage isomerism occurs with *ambidentate* ligands that are capable of coordinating in more than one way. The best known cases involve the monodentate ligands: SCN^- / NCS^- and NO_2^- / ONO^-. The only difference is what **atoms the molecular ligands bind to the central ion**. The ligand(s) must have more than one donor atom, but bind to ion in only one place. For example, the (NO_2^-) ion is a ligand that can bind to the central atom through the nitrogen or the oxygen atom, but cannot bind to the central atom with both oxygen and nitrogen at once, in which case it would be called a **polydentate ligand** rather than an **ambidentate ligand**.

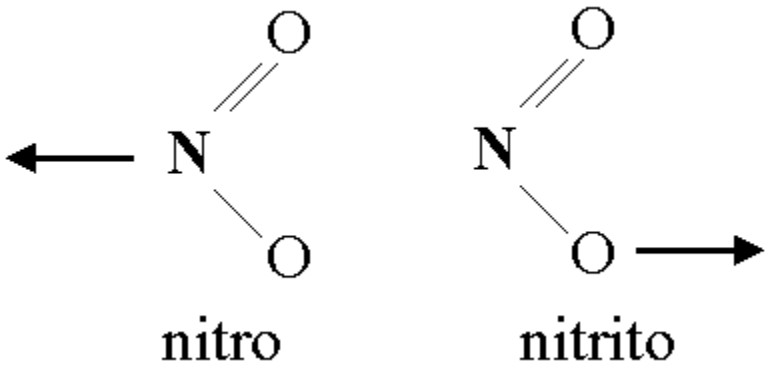


Figure 24.4.5: Linkage Isomerism in the NO_2 ligand. This occurs when a particular ligand is capable of coordinating to a metal in two different and distinct ways. from Angel C. de Dios.

As with all structural isomers, the formula of the complex is unchanged for each isomer, but the properties may differ. The names used to specify the changed ligands are changed as well. For example, the NO_2^- ion is called *nitro* when it binds with the N atom and is called *nitrito* when it binds with the O atom.

Example 24.4.3: Linkage Isomerization

The cationic cobalt complex $[Co(NH_3)_5(NO_2)]Cl_2$ exists in two separable linkage isomers of the complex ion: $(NH_3)_5(NO_2)]^{2+}$.

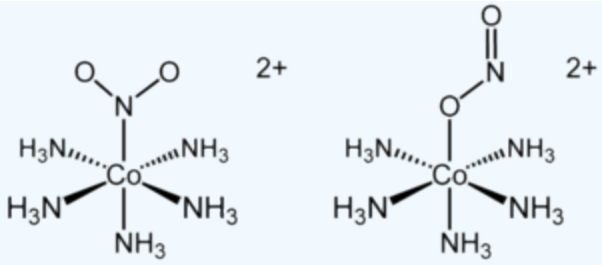


Figure 24.4.6: Linkage Isomerization. (left) The nitro isomer (Co-NO2) and (right) the nitrito isomer (Co-ONO)

When donation is from nitrogen to a metal center, the complex is known as a *nitro-* complex and when donation is from one oxygen to a metal center, the complex is known as a *nitrito-* complex. An alternative formula structure to emphasize the different coordinate covalent bond for the two isomers

- $[Co(ONO)(NH_3)_5]Cl$: the *nitrito* isomer -O attached
- $[Co(NO_2)(NH_3)_5]Cl$: the *nitro* isomer - N attached.

Another example of an ambidentate ligand is thiocyanate, SCN^-, which can attach to the transition metal at either the sulfur atom or the nitrogen atom. Such compounds give rise to linkage isomerism. Other ligands that give rise to linkage isomers include selenocyanate, $SeCN^-$ – isoselenocyanate, $NCSe^-$ and sulfite, $SO_3{}^{2-}$.

Exercise 24.4.3

Are $[FeCl_5(NO_2)]^{3-}$ and $[FeCl_5(ONO)]^{3-}$ complex ions linkage isomers of each other?

Answer available at the end of this section.

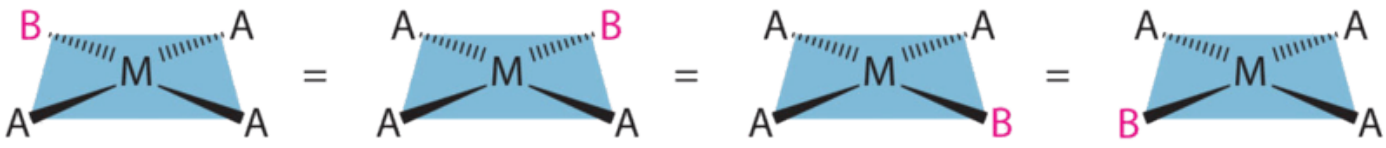
Class 2: Geometric Isomers

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

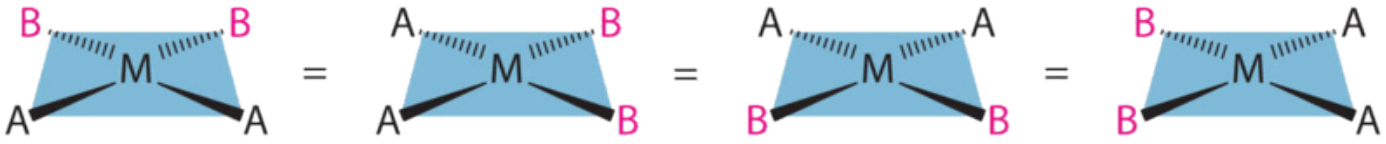
Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

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:

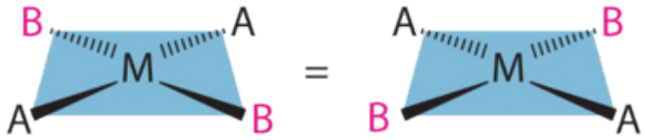


MA_3B square planar complex

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:

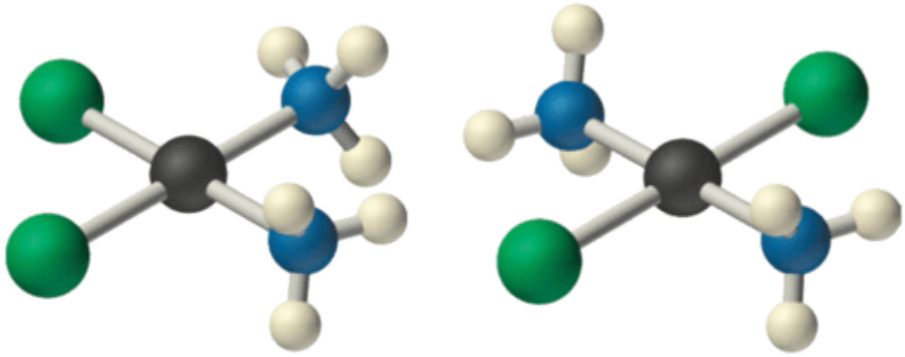


MA_2B_2 square planar complex, *cis* isomer



MA_2B_2 square planar complex, *trans* isomer

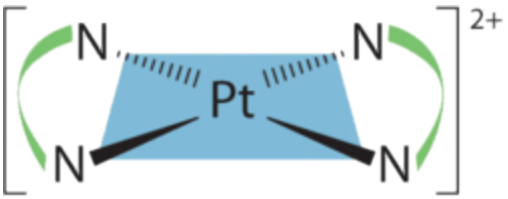
Because there is no way to convert the cis structure to the trans by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space. Probably the best-known examples of cis and trans isomers of an MA_2B_2 square planar complex are cis-$Pt(NH_3)_2Cl_2$, also known as cisplatin, and trans-$Pt(NH_3)_2Cl_2$, which is actually toxic rather than therapeutic.



cis-$Pt(NH_3)_2Cl_2$ *trans*-$Pt(NH_3)_2Cl_2$

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:



$[Pt(en)_2]^{2+}$

Exercise 24.4.4

Draw the cis and trans isomers of the following compounds:

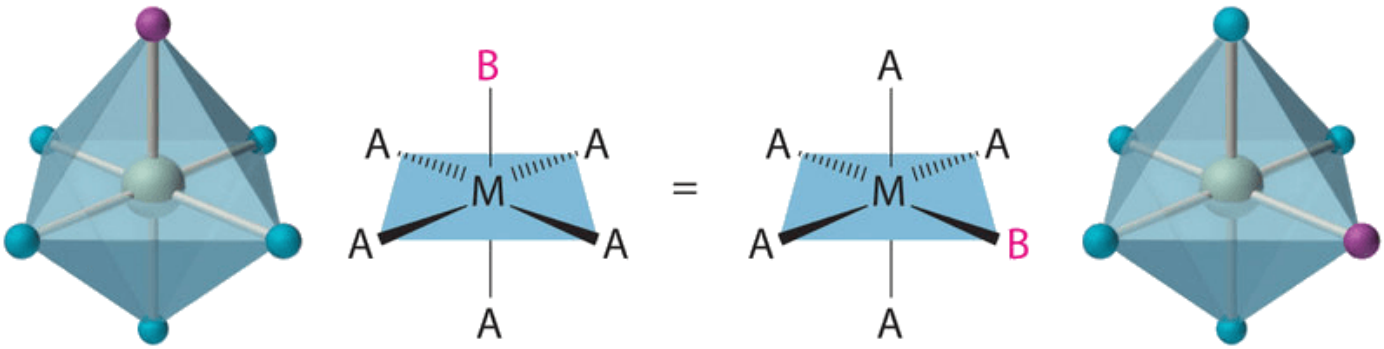
a. $(NH_3)_2IrCl(CO)$
b. $(H_3P)_2PtHBr$
c. $(AsH_3)_2PtH(CO)$

Exercise 24.4.5

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.

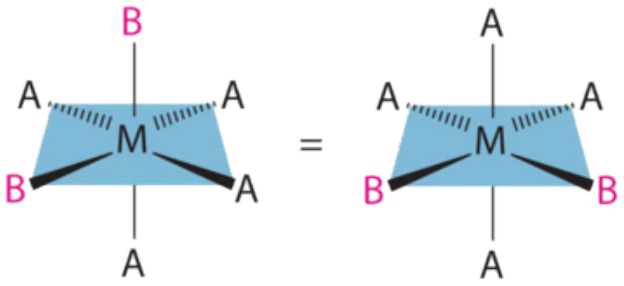
Octahedral Isomers

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:

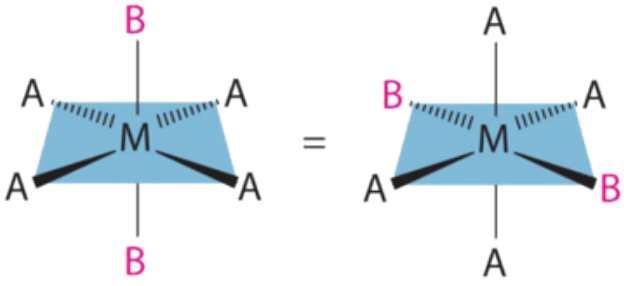


MA_5B octahedral complex

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:

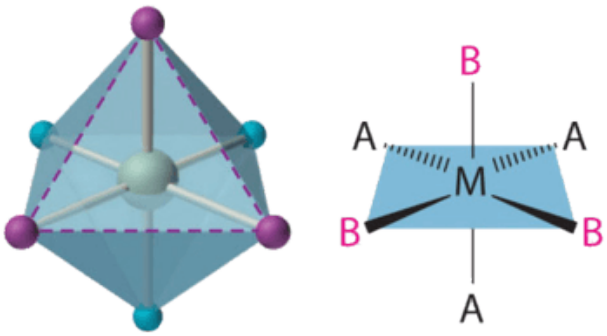


MA_4B_2 octahedral complex, *cis* isomer

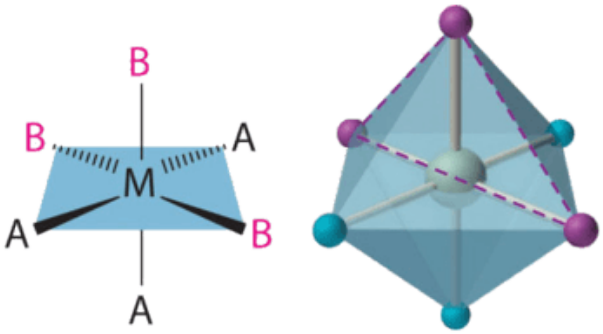


MA_4B_2 octahedral complex, *trans* isomer

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 24.4.4

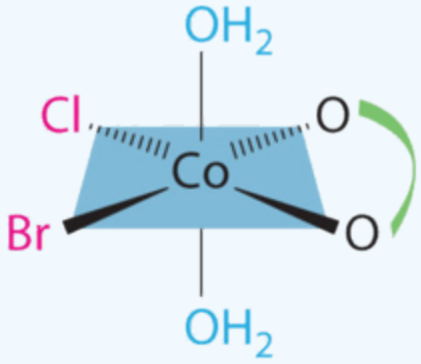
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Solution

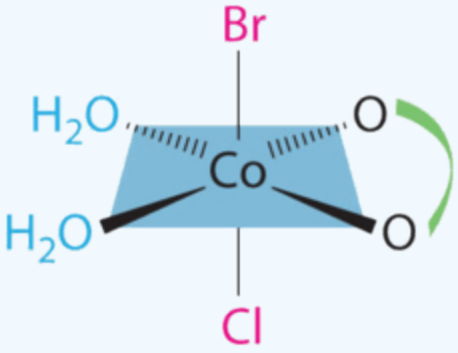
Given: formula of complex

Asked for: structures of geometrical isomers

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:

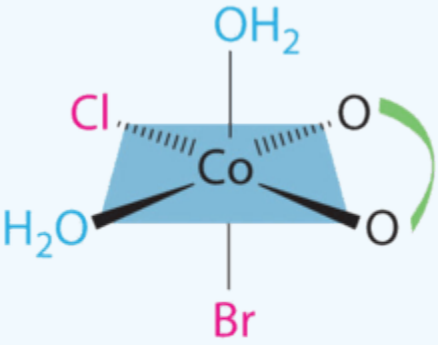


H_2O's *trans*

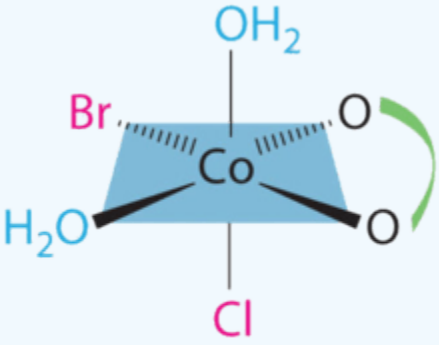


Br, Cl *trans*

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 24.4.6

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer available at the end of this section.

Summary

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**. 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.

Table 24.4.1 emphasizes the key differences of the three classes of structural isomers discussed below. The highlighted ions are

the ions that switch or change somehow to make the type of structural isomer it is.

Table 24.4.1*: Overview of Structural Isomer Classes*

Structural Isomer	Examples
Ionization	$[CoBr(H_2O)_5]^+Cl^-$ and $[CoCl(H_2O)_5]^+Br^-$
Coordination	$[Zn(NH_3)_4]^+[CuCl_4]^{2-}$ and $[Cu(NH_3)_4]^+[ZnCl_4]^{2-}$
Linkage	$[Co(NO_2)_6]^{3-}$ and $[Co(ONO)_6]^{3-}$

References

1. Petrucci, Harwood, Herring, and Madura. General Chemistry: Principles and Modern Applications: Ninth Edition. New Jersey: Pearson, 2007.
2. Atkins, Peter, and Loretta Jones. Chemical Principles: The Quest for Insight: Fourth Edition. W. H. Freeman and Company, 2008. Print.

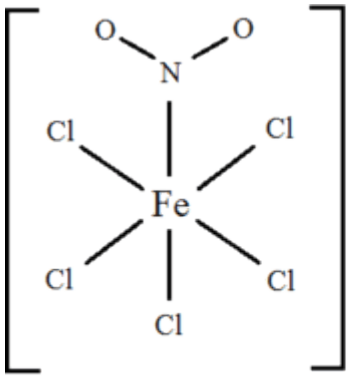
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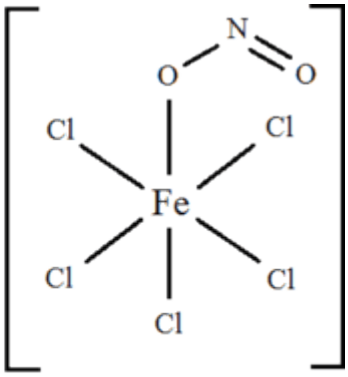
Answers

Exercise 24.4.3

Here, the difference is in how the ligand bonds to the metal. In the first isomer, the ligand bonds to the metal through an electron pair on the nitrogen. In the second isomer, the ligand bonds to the metal through an electron pair on one of the oxygen atoms. It's easier to see it:

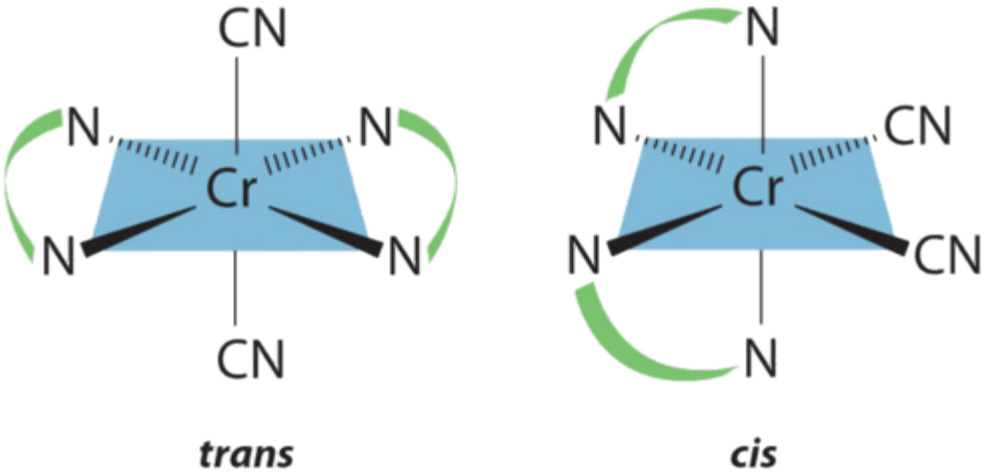


$[FeCl_5(NO_2)]^{3-}$



$[FeCl_5(ONO)]^{3-}$

Exercise 24.4.6



Two geometrical isomers are possible: *trans* and *cis*.

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24.5: Bonding in Complex Ions: 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 $24.5.1a$). 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 $24.5.1b$, 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.

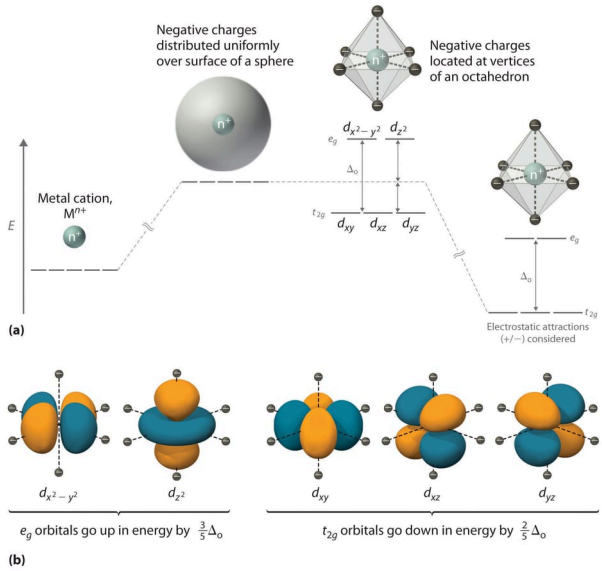


Figure 24.5.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase 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. (CC BY-SA-NC; anonymous by request)

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

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0. \tag{24.5.1}$$

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 24.5.1*a*).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 24.5.1 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 24.5.2, 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.

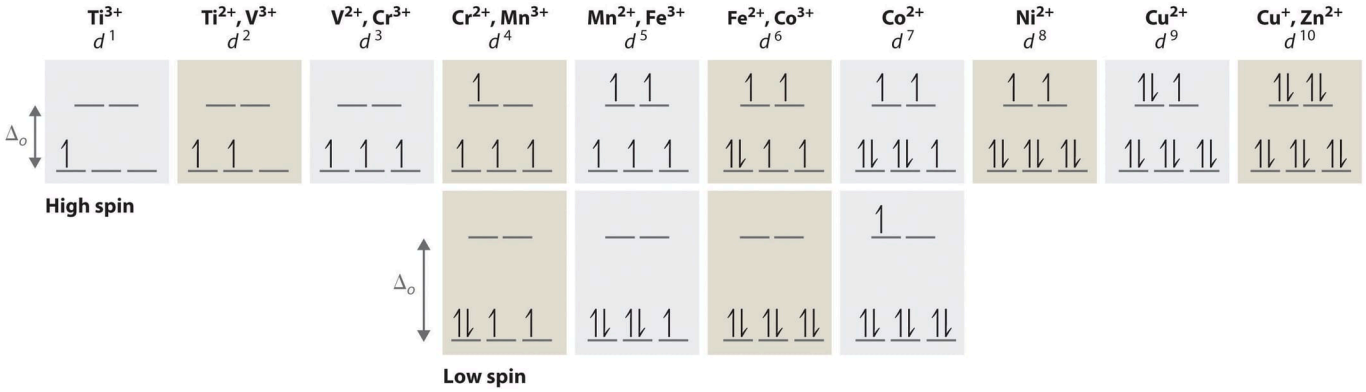


Figure 24.5.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed. (CC BY-SA-NC; anonymous by request)

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 24.5.1.

Table 24.5.1: 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).

Factor 1: 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}.

Factor 2: 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.

Factor 3: 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 $24.5.1$ 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.

Example $24.5.1$

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 24.5.1

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. $[PtCl_4]^{2-}$

Answer a available at the end of this section.

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 24.5.2 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 24.5.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
	t_{2g}	e_g		t_{2g}	e_g	
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.

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.

Answers

Exercise 24.5.1

octahedral; high spin; five

square planar; low spin; no unpaired electrons

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24.6: Magnetic Properties of Coordination Compounds and Crystal Field Theory

The magnetic properties of a compound can be determined from its electron configuration and the size of its atoms. Because magnetism is generated by electronic spin, the number of unpaired electrons in a specific compound indicates how magnetic the compound is. In this section, the magnetism of the d-block elements (or transition metals) are evaluated. These compounds tend to have a large number of unpaired electrons.

Introduction

An interesting characteristic of transition metals is their ability to form magnets. Metal complexes that have unpaired electrons are magnetic. Since the last electrons reside in the d orbitals, this magnetism must be due to having unpaired d electrons. The spin of a single electron is denoted by the quantum number m_s as +(1/2) or –(1/2). This spin is negated when the electron is paired with another, but creates a weak magnetic field when the electron is unpaired. More unpaired electrons increase the paramagnetic effects. The electron configuration of a transition metal (d-block) changes in a coordination compound; this is due to the repulsive forces between electrons in the ligands and electrons in the compound. Depending on the strength of the ligand, the compound may be paramagnetic or diamagnetic.

Bulk Magnetism: Ferromagnetism

Ferromagnetism is the basic mechanism by which certain materials (such as iron) form permanent magnets. This means the compound shows permanent magnetic properties rather than exhibiting them only in the presence of a magnetic field (Figure 24.6.1). In a ferromagnetic element, electrons of atoms are grouped into domains in which each domain has the same charge. In the presence of a magnetic field, these domains line up so that charges are parallel throughout the entire compound. Whether a compound can be ferromagnetic or not depends on its number of unpaired electrons and on its atomic size.

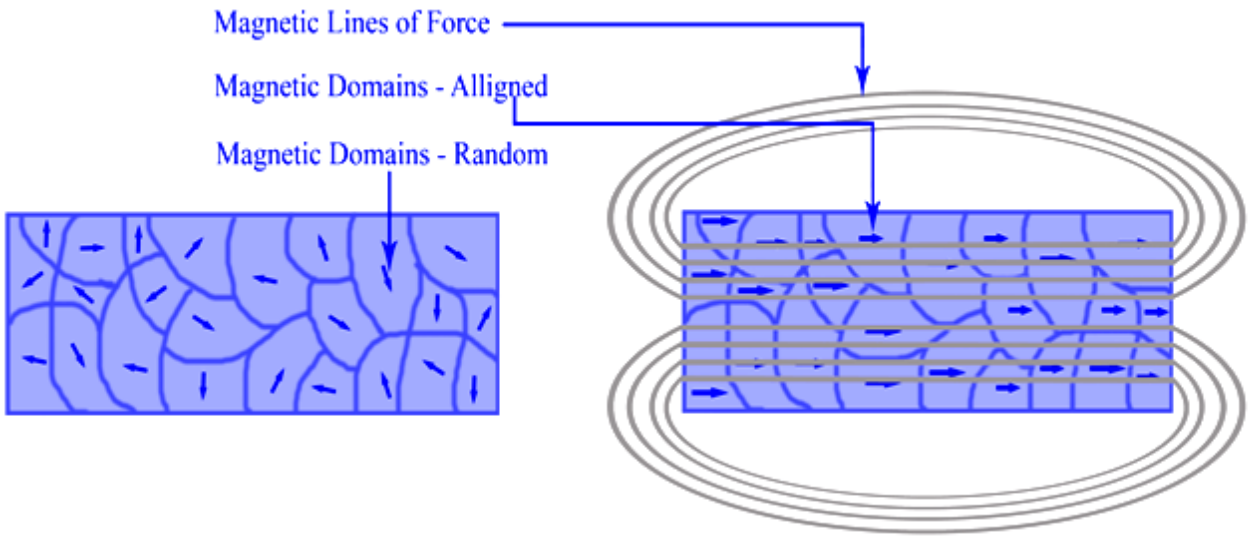


Figure 24.6.1: Ferromagnetism (a) nonmagnatized material and (2) Magnetized material with corresponding magnetic fields shown.

Ferromagnetism, the permanent magnetism associated with nickel, cobalt, and iron, is a common occurrence in everyday life. Examples of the knowledge and application of ferromagnetism include Aristotle's discussion in 625 BC, the use of the compass in 1187, and the modern-day refrigerator. Einstein declared that electricity and magnetism are inextricably linked in his theory of special relativity.

Magnetic Moments of Molecules and Ions

Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as O_2 that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic. Molecules such as N_2 and ions such as Na^+ and $[Fe(CN)_6]^{4-}$ that contain no unpaired electrons are diamagnetic. Diamagnetic substances have a slight tendency to be repelled by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion paramagnetic. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Therefore, the observed magnetic moment is used to determine the number of unpaired electrons present. The measured magnetic moment of low-spin d^6 $[Fe(CN)_6]^{4-}$ confirms that iron is diamagnetic, whereas high-spin d^6 $[Fe(H_2O)_6]^{2+}$ has four unpaired electrons with a magnetic moment that confirms this arrangement.

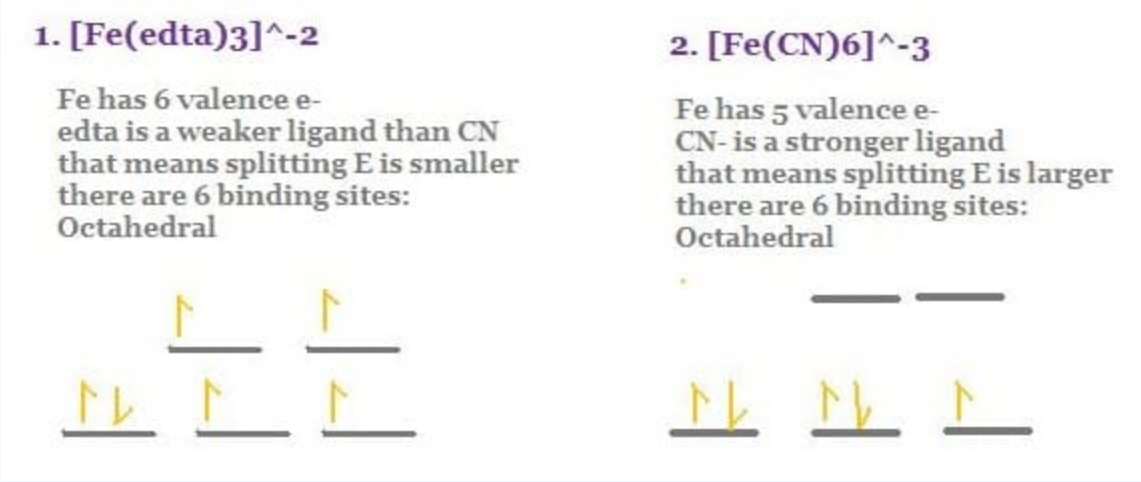
Hunds' Rule states that electrons fill all available orbitals with single electrons before pairing up, while maintaining parallel spins (paired electrons have opposing spins). For a set of five degenerate d-orbitals in an uncomplexed metal atom, electrons fill all orbitals before pairing to conserve pairing energy. With the addition of ligands, the situation is more complicated. The splitting energy between the d-orbitals increases the energy required to place single electrons into the higher-energy orbitals. Once the lower-energy orbitals have been half-filled (one electron per orbital), an electron can either be placed in a higher-energy orbital or paired with an electron in a lower-energy orbital. The strength of the ligands determine which option is chosen. If the splitting energy is greater than the pairing energy, the electrons will pair up; if the pairing energy is greater, unpaired electrons will occupy higher energy orbitals. In other words, with a strong-field ligand, low-spin complexes are usually formed; with a weak-field ligand, a high-spin complex is formed.

Low-spin complexes contain more paired electrons because the splitting energy is larger than the pairing energy. These complexes, such as $[Fe(CN)_6]^{3-}$, are more often diamagnetic or weakly paramagnetic. Likewise, high-spin complexes usually contain more unpaired electrons because the pairing energy is larger than the splitting energy. With more unpaired electrons, high-spin complexes are often paramagnetic. The unpaired electrons in paramagnetic compounds create tiny magnetic fields, similar to the domains in ferromagnetic materials. The strength of the paramagnetism of a coordination complex increases with the number of unpaired electrons; a higher-spin complex is more paramagnetic. The occurrence and relative strength of paramagnetism can be predicted by determining whether the compound is coordinated to a weak field ligand or a strong field ligand.

Example 24.6.1

Which ligand generates a stronger magnetic complex ion when bound to Fe^{+2}: EDTA or CN^-?

Solution



Since $[Fe(EDTA)_3^{-2}]$ has more unpaired electrons than $[FeCN_6^{-3}]$, it is more paramagnetic.

Example 24.6.2

ZnI_4 have eight valence electrons. If it is found to be diamagnetic, then does it occupy a tetrahedral or square plan geometry?

Solution

The splitting pattern for the two geometries differ and hence the electron configuration from adding the eight electrons also differ.



The tetrahedral geometry has two unpaired electrons and the square planer geometry has zero. Since ZnI_4 is diamagnetic, it must have a square planar geometry.

Exercise 24.6.1

For each of the following coordination complexes, identify if it is paramagnetic or diamagnetic?

a. octahedral, low spin, d^4,
b. octahedral, low spin, d^6,
c. tetrahedral, low spin, d^4
d. square planar, low spin, d^8

Measuring the Strength of Magnetism

The Gouy balance is used to measure paramagnetism by suspending the complex in question against an equivalent weight with

access to a magnetic field. In principle, a magnetic measurement can be done very simply. All it takes is a balance and a magnetic field. We all know how a balance works. In a simple model from an earlier time, we place the sample in one pan. The balance tips over. We find the appropriate weight - a little piece of carefully prepared metal, certified by some bureau of standards. The balance balances. The masses in the two pans must be equal.

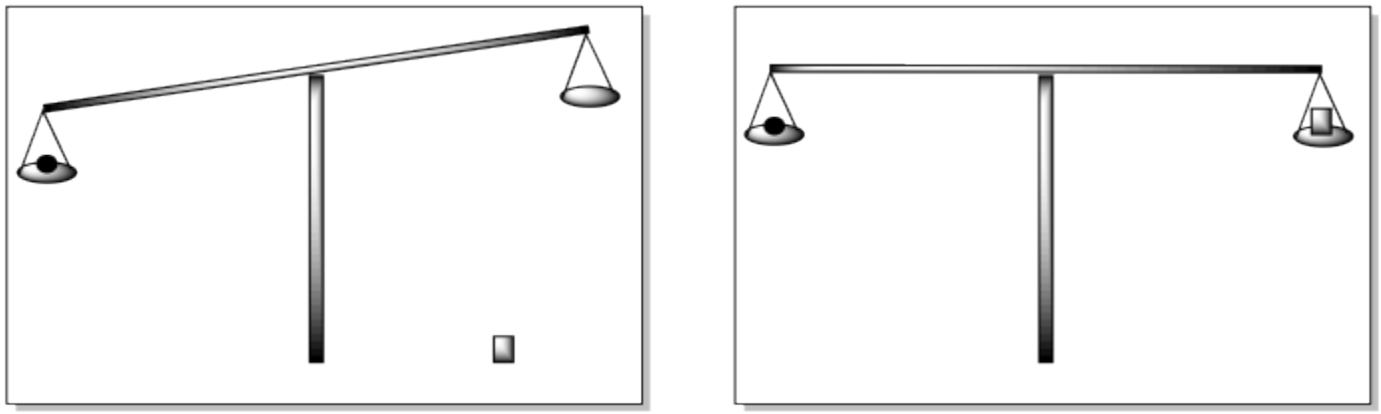


Figure 24.6.2: A typical mass balance used to measure mass by comparing to a known mass.

With a Gouy balance, the same idea applies, but we throw in a magnetic field, too. Even when it should be balanced, the balance tips, because of an attraction to the magnetic field. We need to find another weight that will get the balance even again. The weight needed to balance the scale is proportional to the attraction of the material to the magnetic field.

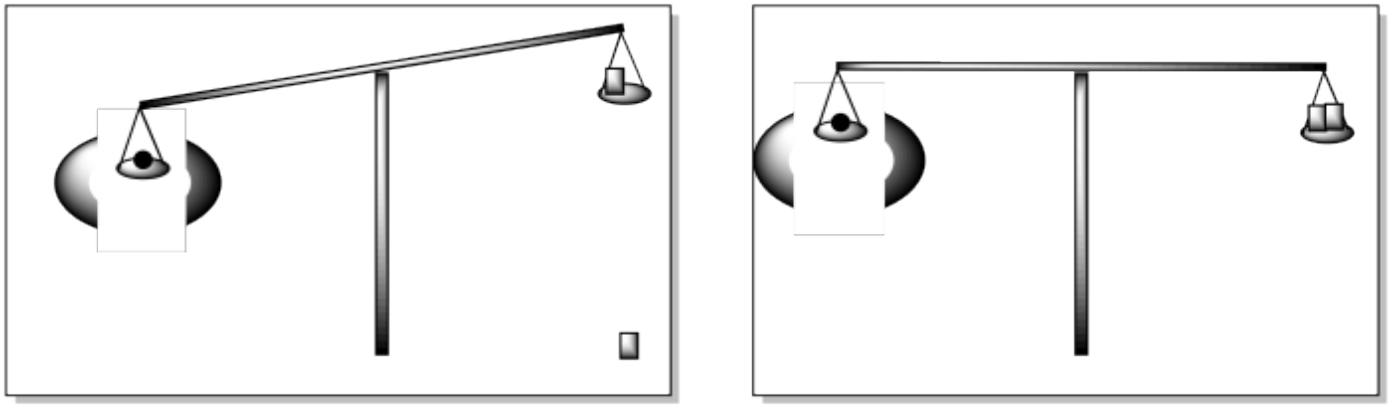


Figure 24.6.3: A Gouy balance measure the strength of a magnet by comparing to the gravitational force of a known mass.

If the compound is paramagnetic, it will be pulled visibly towards the electromagnet, which is the distance proportional to the magnitude of the compound's paramagnetism. If the compound, however, is diamagnetic, it will not be pulled towards the electromagnet, instead, it might even slightly be repelled by it. This will be proven by the decreased weight or the no change in weight. The change in weight directly corresponds to the amount of unpaired electrons in the compound.

References

1. Petrucci [chapter 23. p. 968 and chapter 24 section 24-5].
2. Johnson, Ronald C. and Basolo, Fred, "Coordination Chemistry: The Chemistry of Metal Complexes, W. A. Benjamin, Inc. pp40-44. 1964
3. Jones, Mark M. Elementary Coordination Chemistry Prentice-Hall, Inc. 1964

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24.7: Color and the Colors of Complexes

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow (Figure $24.7.1$).

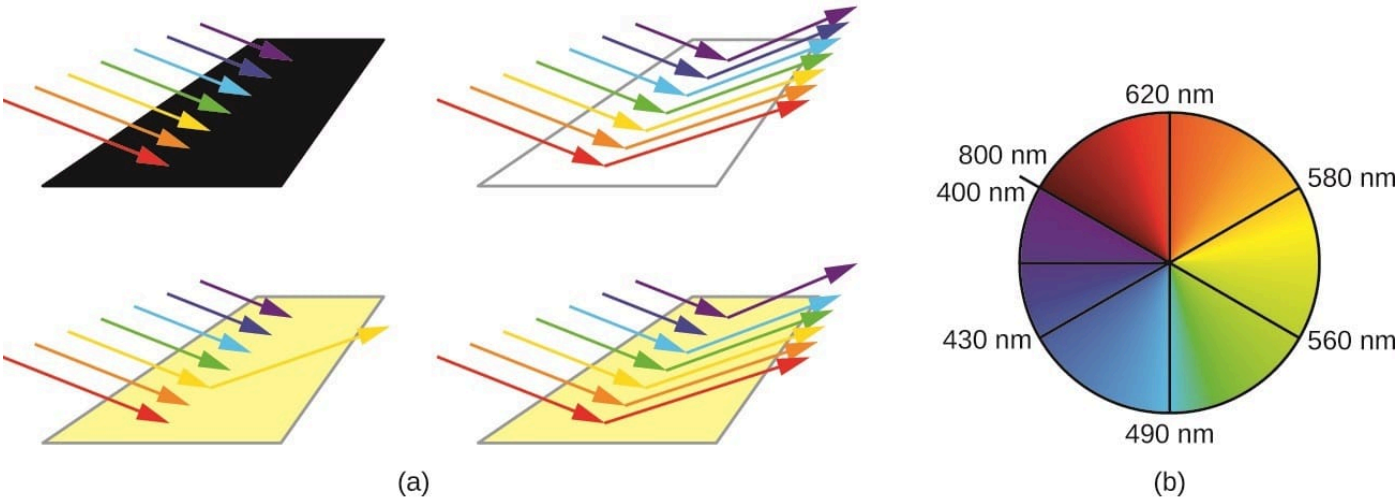


Figure $24.7.1$: (a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (CC BY 4.0; OpenStax)

The blue color of the $[Cu(NH_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (Figure $24.7.2$). If white light (ordinary sunlight, for example) passes through $[Cu(NH_3)_4]SO_4$ solution, some wavelengths in the light are absorbed by the solution. The $[Cu(NH_3)_4]^{2+}$ 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 a $[Cu(NH_3)_4]SO_4$ solution.

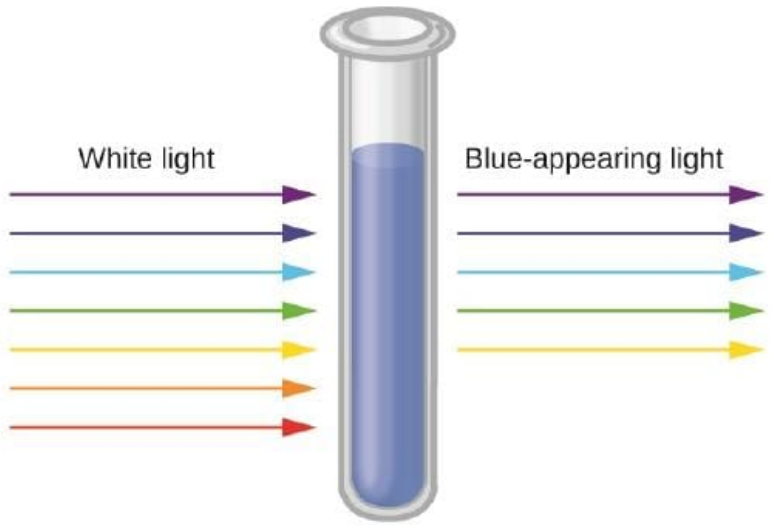


Figure 24.7.2: A solution of $[Cu(NH_3)_4]^{2+}$ ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue. (CC BY 4.0; OpenStax)

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.

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 complementary color wheel.



Figure 24.7.3: The partially filled d orbitals of the stable ions $Cr^{3+}(aq)$, $Fe^{3+}(aq)$, and $Co^{2+}(aq)$ (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)

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 24.7.4). 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.

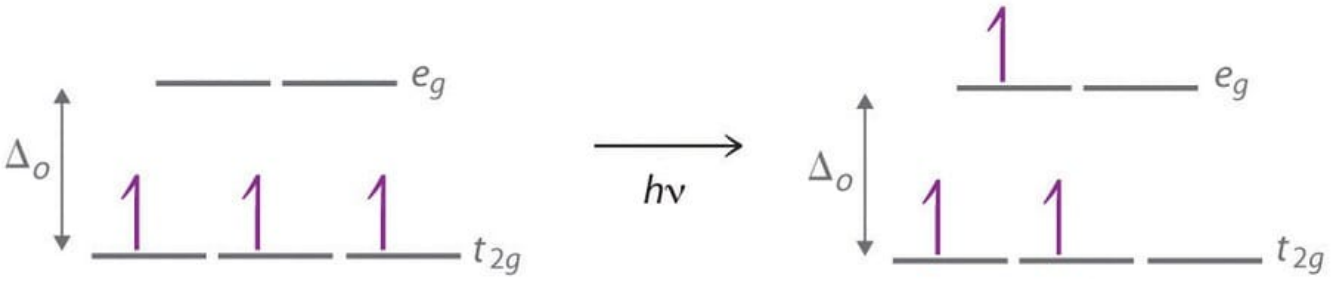


Figure 24.7.4: In a d–d transition of an octahedral complex, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

Example 24.7.1: Colors of Complexes

The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single *d* electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_o and occurs at 499 nm. Calculate the value of Δ_o in Joules and predict what color the solution will appear.

Solution

We can convert wavelength to frequency:

$$\begin{aligned}\nu &= \frac{c}{\lambda} \\ &= \frac{3.00 \times 10^8\, m/s}{(499\ \cancel{pm}) \times \left(\frac{1\, m}{10^9\ \cancel{pm}}\right)} \\ &= 6.01 \times 10^{14} s^{-1} = 6.01 \times 10^{14}\, Hz\end{aligned}$$

And then using Planck's equation that related the frequency of light to energy

$$E = h\nu$$

so

$$\begin{aligned}E &= (6.63 \times 10^{-34}\text{J·s}) \times (6.01 \times 10^{14}\, Hz) \\ &= 3.99 \times 10^{-19}\, J\end{aligned}$$

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

Note: This is the energy for one transition (i.e., in one complex). If you want to calculate the energy in J/mol, then you have to multiply this by Avogadro's number (N_A).

Exercise 24.7.1

A complex that appears green, absorbs photons of what wavelengths?

Answer available at the end of this section.

Color Depends on Oxidation State

Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in Figure 24.7.4, different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link 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

Watch this video of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

Color Depends on Ligand Field

The specific ligands coordinated to the metal center also influence the color of coordination complexes. 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. For example, the iron(II) complex $[Fe(H_2O)_6]SO_4$ appears blue-green because the high-spin complex absorbs photons in the red wavelengths (Figure 24.7.5). In contrast, the low-spin iron(II) complex $K_4[Fe(CN)_6]$ appears pale yellow because it absorbs higher-energy violet photons.

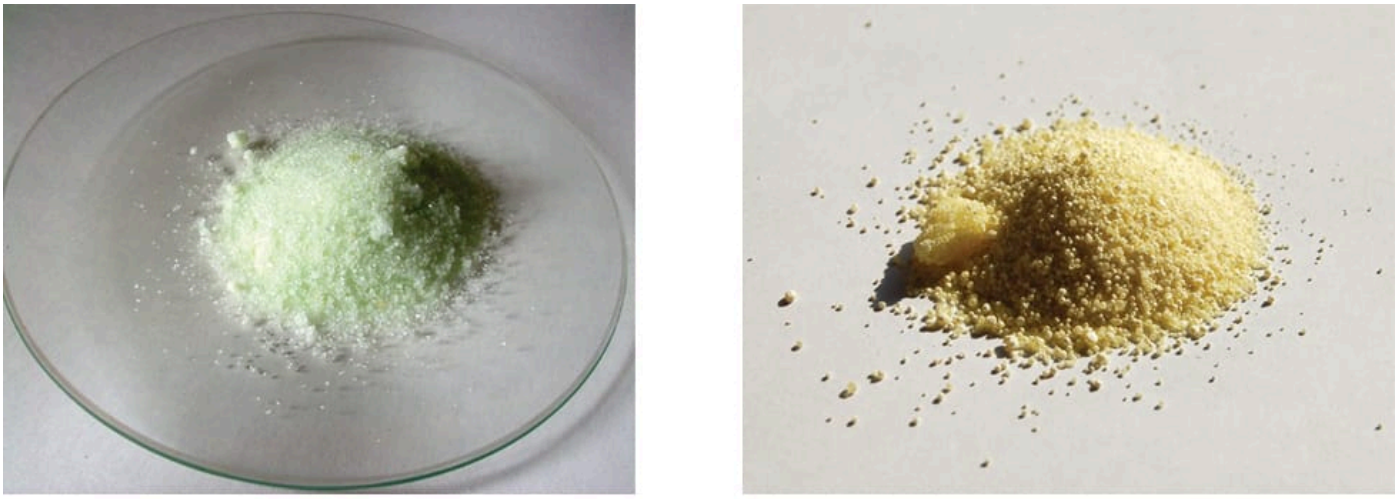


Figure 24.7.5: Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain d^6 iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum. (CC BY 4.0; OpenStax)

In general, strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom (large Δ_{oct}). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

Strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom and transition metal coordination compounds with these ligands are typically yellow, orange, or red because they absorb higher-energy violet or blue light. Coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

Example 24.7.2: Matching Colors to Ligand Fields

Identify the color (either blue, green, yellow, or orange) for the following complex ions formed with Co^{3+}:

a. $[Co(CN)_6]_3^{-2}$
b. $[Co(NH_3)_6]_3^{3+}$
c. $[CoF_6]_3^{-4}$
d. $[Co(H_2O)_6]^{3+}$

Solution

Each of these complex ions has the same metal with the same oxidation state, so the ligand field is the relevant factors. Each of the complex ions also has an octahedral ligand field, so we only need to compare the strength of the ligands in determining Δ_o, which is determined by the spectrochemical series.

The ligands for each complex ions are: (a) CN^-, (b) NH_3, (c) F^- and (d) H_2O, which are ranked in increasing Δ_o magnitude:

$$F^- < H_2O < NH_3 < CN^- \tag{24.7.1}$$

The relationship between the Δ_o and the energy of the photons are absorbed in the d-d transition of Co^{3+} is given by equating Planck's equation to the crystal field splitting parameter:

$$E = h\nu = \frac{hc}{\lambda} = \Delta_o \tag{24.7.2}$$

Now, we need to get a relative correlation between observed color (to the eye) and the wavelength of the light that is absorbed. From the complementary color wheel in Figure 24.7.1 we get the following relationships (arranged from highest energy absorbed to lowest):

- 400-nm Violet light absorbed → Green-yellow observed
- 430-nm Blue light absorbed → Orange observed
- 450-nm Blue light absorbed → Yellow observed
- 490-nm Blue-green light absorbed → Red observed
- 570-nm Yellow-green light absorbed → Violet observed
- 580-nm Yellow light absorbed → Dark blue observed
- 600-nm Orange light absorbed → Blue observed
- 650-nm Red light absorbed → Green observed

Of the four possible colors given in the problem (blue, green, yellow, and orange), the corresponding colors that are absorbed are (600 nm, 650 nm, 450 nm, and 430, respectively). From Equation 24.7.2, the smaller λ of absorbed light corresponds to the higher energy photons, so we would correlate the four wavelengths of absorbing photons in terms of increasing energy to observed color:

$$\underbrace{650\,nm}_{green} < \underbrace{600\,nm}_{blue} < \underbrace{450\,nm}_{yellow} < \underbrace{430\,nm}_{orange} \tag{24.7.3}$$

Now, just correlate the ranking in Equation 24.7.3 to the ranking in Equation 24.7.1:

$$\underbrace{F^-}_{green} < \underbrace{H_2O}_{blue} < \underbrace{NH_3}_{yellow} < \underbrace{CN^-}_{orange}$$

and more specifically in terms of the original question

$$\underbrace{[CoF_6]_3^{-4}}_{green} < \underbrace{[Co(H_2O)_6]^{3+}}_{blue} < \underbrace{[Co(NH_3)_6]_3^{3+}}_{yellow} < \underbrace{[Co(CN)_6]_3^{-2}}_{orange}$$

Exercise 24.7.1

If a complex ion $[M(NH_3)_6]^{2+}$ is red in solution, which of the following ligands, after a ligand exchange reaction to substitute for the ammine ligands, may shift the solution to be orange? More than one answer is possible.

$$Cl^-, CN^-, CO, F^- \; H_2O, I^-, en, NO_2^-, OH^-, SCN^-$$

Answer available at the end of this section.

A coordination compound of the Cu^+ ion has a d^{10} configuration, and all the e_g orbitals are filled. To excite an electron to a higher level, such as the 4*p* orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing $[Cu(CN)_2]^-$, for example, is colorless. On the other hand, octahedral Cu^{2+} complexes have a vacancy in the e_g orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and Cu^{2+} complexes are almost always colored—blue, blue-green violet, or yellow (Figure 24.7.6). Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.

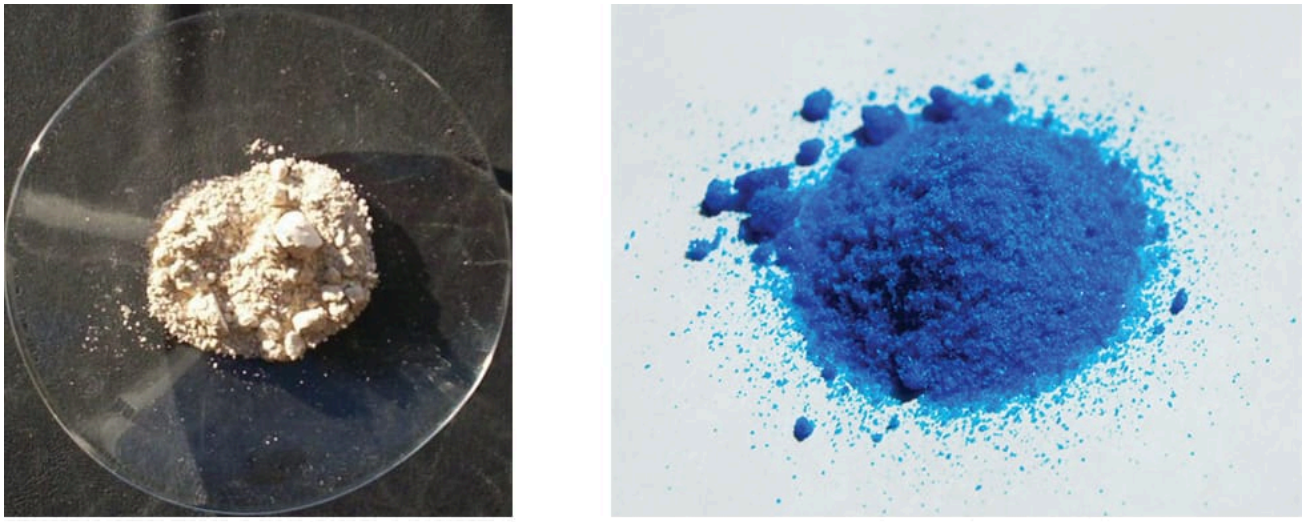


Figure 24.7.6: (a) Copper(I) complexes with d^{10} configurations such as CuI tend to be colorless, whereas (b) d^9 copper(II) complexes such as $Cu(NO_3)_2{\cdot}5H_2O$ are brightly colored. (CC BY 4.0; OpenStax)

Gems

A ruby is a pink to blood-red colored gemstone that consist of trace amounts of chromium in the mineral corundum Al_2O_3. In contrast, emeralds are colored green by trace amounts of chromium within a $Be_3Al_2Si_6O_{18}$ matrix. 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.

The absorbance spectrum of a ruby is shown Figure $24.7.7; left$. The number and positions of the peaks in the spectrum is determined by the electronic structure of the compound, which in this case depends upon the identity of the metal and the identities, number, and geometry of the surrounding ions. Crystal field theory may be used to predict the electronic structure and thus the absorbance spectrum. If white light is shown on the gem, the absorbance spectrum indicates which wavelengths of light are removed. In this case, there are strong bands centered at 414 and 561 nm. These wavelengths correspond with blue and yellow-green light, respectively. For the most part, these colors are not present in the light reaching ones eyes. An alternative way to express this concept is to recognize that the spectrum of light reaching the eye is the product of the spectrum of the incident light (white light) and the **transmittance spectrum**. For this ruby, the transmittance spectrum has a peak at 481 nm and a broad plateau past 620 nm. (Note that there is significant attenuation of the light across the entire spectrum.) Thus only light with wavelengths near 481 nm (cyan) and greater than 620 nm (red) reach the eye.

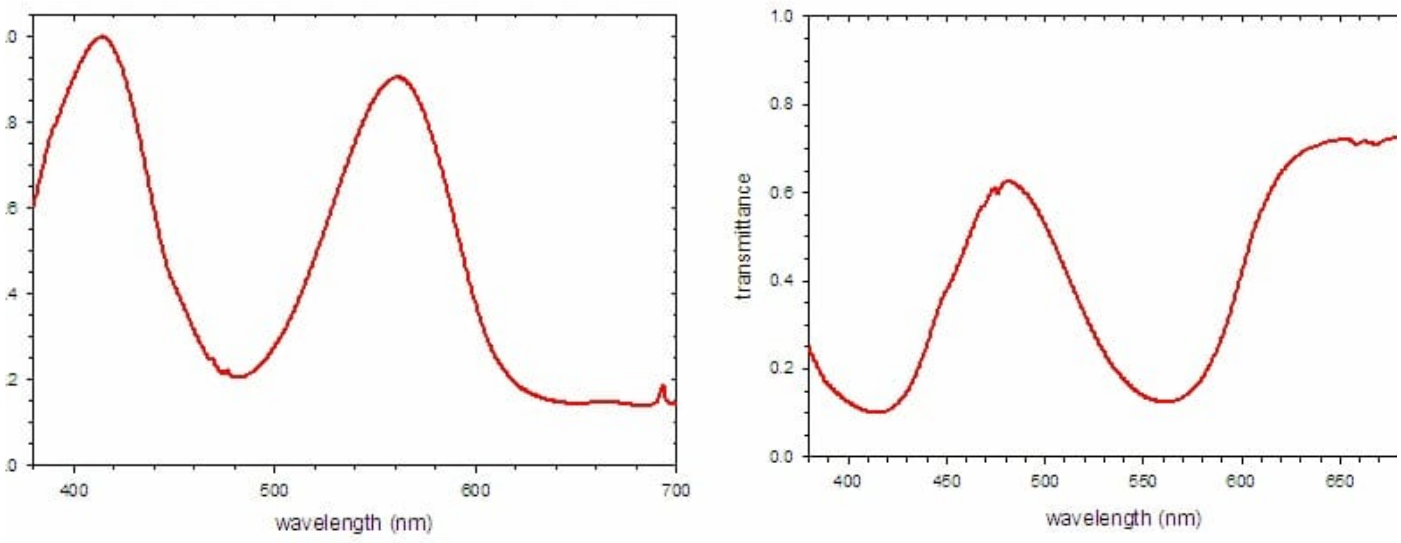
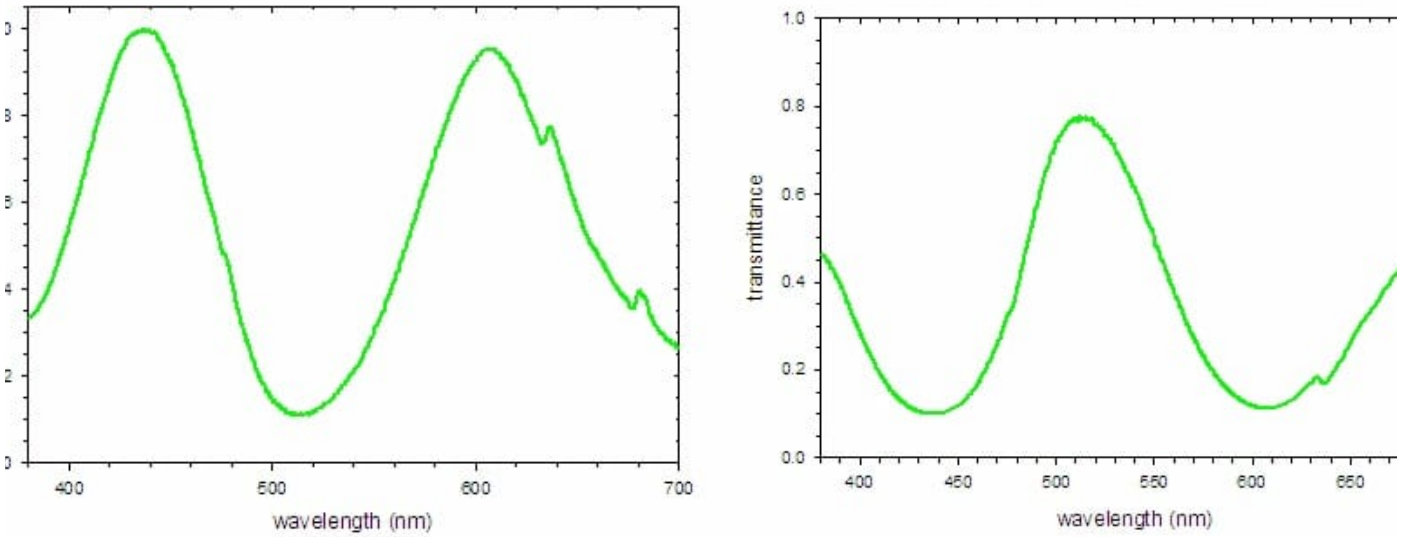


Figure $24.7.7$: (left) Absorbance spectrum of a ruby from Chanthaburi, Thailand. (right) corresponding Transmittance spectrum of a ruby from Chanthaburi, Thailand. Data obtained from the Caltech Mineral Spectroscopy Server

A similar analysis of the spectrum of an emerald is possible. The absorbance spectrum (Figure $24.7.8; left$) shows strong bands at 438 and 606 nm, which remove blue and orange light, respectively. The light that is not absorbed is shown by the transmittance spectrum, which indicates the dominant band of light reaching the eye is centered at 512 nm (green light) with smaller contributions from the far blue and red portions of the spectrum. This combination of wavelengths produces a deep green color.



(left) Absorbance spectrum of an emerald from Malyshevo, Ural, Russia. (right) Corresponding transmittance spectrum of the emerald from Malyshevo, Ural, Russia. Data obtained from the Caltech Mineral Spectroscopy Server

Summary

When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the *d* orbitals often allows photons in the visible range to be absorbed.

Contributors and Attributions

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- Prof. David Blauch (Davidson College)

Answers

Exercise $24.7.1$

red, 620–800 nm

Exercise $24.7.1$

Shifting from red to orange is an increase in Δ_o, so those ligands that are stronger field ligands than NH_3 in the list (deterimined via the spectrochemical series) are CN^-, CO, en, and NO_2^-.

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24.8: Aspects of Complex-Ion Equilibria

Learning Objectives

- To be introduced to complex ions, including ligands.

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.



Figure 24.8.1: 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 https://www.youtube.com/watch?v=IQNcLH6OZK0.

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 24.8.1. 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.

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 Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

$$Cu^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)]^{2+}(aq) \qquad \text{(step 1)}$$

with

$$K_1 = \frac{[\mathrm{Cu(NH_3)}]^{2+}\,(\mathrm{aq})}{[\mathrm{Cu}^{2+}\,(\mathrm{aq})][\mathrm{NH_3}\,(\mathrm{aq})]}$$

$$[\mathrm{Cu(NH_3)}]^{2+}\,(\mathrm{aq}) + \mathrm{NH_3}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Cu(NH_3)_2}]^{2+}\,(\mathrm{aq}) \qquad \text{(step 2)}$$

with

$$K_2 = \frac{[\mathrm{Cu(NH_3)_2}]^{2+}\,(\mathrm{aq})}{[[\mathrm{Cu(NH_3)}]^{2+}\,(\mathrm{aq})][\mathrm{NH_3}\,(\mathrm{aq})]}$$

$$[\mathrm{Cu(NH_3)_2}]^{2+}\,(\mathrm{aq}) + \mathrm{NH_3}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Cu(NH_3)_3}]^{2+}\,(\mathrm{aq}) \qquad \text{(step 3)}$$

with

$$K_3 = \frac{[\mathrm{Cu(NH_3)_3}]^{2+}\,(\mathrm{aq})}{[[\mathrm{Cu(NH_3)_2}]^{2+}\,(\mathrm{aq})][\mathrm{NH_3}\,(\mathrm{aq})]}$$

$$[\mathrm{Cu(NH_3)_3}]^{2+}\,(\mathrm{aq}) + \mathrm{NH_3}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Cu(NH_3)_4}]^{2+}\,(\mathrm{aq}) \qquad \text{(step 4)}$$

with

$$K_4 = \frac{[\mathrm{Cu(NH_3)_4}]^{2+}\,(\mathrm{aq})}{[[\mathrm{Cu(NH_3)_3}]^{2+}\,(\mathrm{aq})][\mathrm{NH_3}\,(\mathrm{aq})]}$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.

$$\mathrm{Cu}^{2+}\,(\mathrm{aq}) + 4\,\mathrm{NH_3}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Cu(NH_3)_4}]^{2+}\,(\mathrm{aq}) \qquad (24.8.1)$$

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:

$$\begin{aligned} K_\mathrm{f} &= \frac{[\mathrm{Cu(NH_3)_4}]^{2+}]}{[\mathrm{Cu}^{2+}][\mathrm{NH_3}]^4} \\ &= 2.1 \times 10^{13} \\ &= K_1 \times K_2 \times K_3 \times K_4 \end{aligned}$$

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 24.8.1.

*Table 24.8.1: 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

***Reported values are overall formation constants. Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).**

	Complex Ion	Equilibrium Equation	K_f
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}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \diamond [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants. Source: Data from ***Lange's Handbook of Chemistry*****, 15th ed. (1999).**

Example 24.8.1

If 12.5 g of $\mathrm{Cu(NO_3)_2 \cdot 6\,H_2O}$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $\mathrm{Cu^{2+}(aq)}$?

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 $\mathrm{Cu^{2+}(aq)}$ due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 24.8.1 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 (K_f) to calculate the equilibrium concentration of $\mathrm{Cu^{2+}(aq)}$.

Solution

Adding an ionic compound that contains $\mathrm{Cu^{2+}(aq)}$ to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}(aq)$, as shown in Equation 24.8.1 We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of $\mathrm{Cu^{2+}(aq)}$ from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5 \cancel{\text{ g}}\ \mathrm{Cu(NO_3)_2 \cdot 6H_2O} \left(\frac{1\ \text{mol}}{295.65 \cancel{\text{ g}}}\right) \left(\frac{1}{500\ \cancel{\text{mL}}}\right) \left(\frac{1000\ \cancel{\text{mL}}}{1\ \text{L}}\right) = 0.0846\ \text{M}$$

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.

$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

ICE	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	+*x*	+4*x*	–*x*
final	*x*	0.66 + 4*x*	0.0846 – *x*

B Substituting the final concentrations into the expression for the formation constant (K_f) and assuming that $x \ll 0.0846$, which allows us to remove x from the sum and difference,

$$\begin{aligned} K_f &= \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} \\ &= \frac{0.0846 - x}{x(0.66 + 4x)^4} \\ &\approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13} \\ x &= 2.1 \times 10^{-14} \end{aligned}$$

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 2.1×10^{-14} M.

Exercise 24.8.1

The ferrocyanide ion ($[Fe(CN)_6]^{4-}$) is very stable, with a K_f of 1×10^{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.

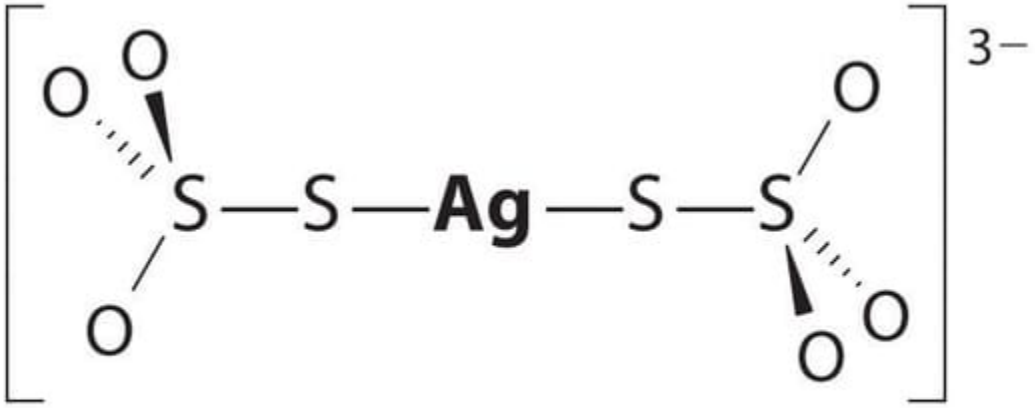
The reaction for the dissolution of silver bromide is as follows:

$$AgBr\,(s) \rightleftharpoons Ag^+\,(aq) + Br^-\,(aq) \tag{24.8.2}$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25°\text{C} \tag{24.8.3}$$

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:

$$Ag^+_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{24.8.4}$$

with

$$K_f = 2.9 \times 10^{13} \tag{24.8.5}$$

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:

$$\begin{aligned}
\mathrm{AgBr(s)} &\rightleftharpoons \mathrm{Ag^+(aq) + Br^-(aq)} \quad K_{\mathrm{sp}} = 5.35 \times 10^{-13} \\
\mathrm{Ag^+(aq) + 2S_2O_3^{2-}(aq)} &\rightleftharpoons \mathrm{[Ag(S_2O_3)_2]^{3-}(aq)} \quad K_{\mathrm{f}} = 2.9 \times 10^{13} \\
\mathrm{AgBr(s) + 2S_2O_3^{2-}(aq)} &\rightleftharpoons \mathrm{[Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)} \quad K = K_{\mathrm{sp}}K_{\mathrm{f}} = 15
\end{aligned}$$

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 24.8.2: Common Ion Effect in Complexation

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. If we let x equal the solubility of AgCl, then at equilibrium

$$[\mathrm{Ag^+}] = [\mathrm{Cl^-}] = \mathrm{x\ M}.$$

Substituting this value into the solubility product expression,

$$\begin{aligned} K_{sp} &= [\mathrm{Ag^+}][\mathrm{Cl^-}] \\ &= (x)(x) \\ &= x^2 \\ &= 1.77 \times 10^{-10} \\ x &= 1.33 \times 10^{-5} \end{aligned}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

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 $x \leq 1.0$:

$$\begin{aligned} K_{sp} &= [\mathrm{Ag^+}][\mathrm{Cl^-}] \\ &= (x)(1.0 + x) \\ &\approx x(1.0) \\ &= 1.77 \times 10^{-10} = x \end{aligned}$$

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. 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:

$$\mathrm{AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)} \quad K_{sp} = 1.77 \times 10^{-10}$$

$$\mathrm{Ag^+aq) + 2Cl^- \rightleftharpoons [AgCl_2]^-} \quad K_f = 1.1 \times 10^5$$

$$\mathrm{AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^-} \quad K = K_{sp}K_f = 1.9 \times 10^{-5}$$

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 $x \leq 1.0$,

$$\begin{aligned} K &= \frac{[\mathrm{AgCl_2^-}]}{[\mathrm{Cl^-}]} \\ &= \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} \\ &= x \end{aligned}$$

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 24.8.2

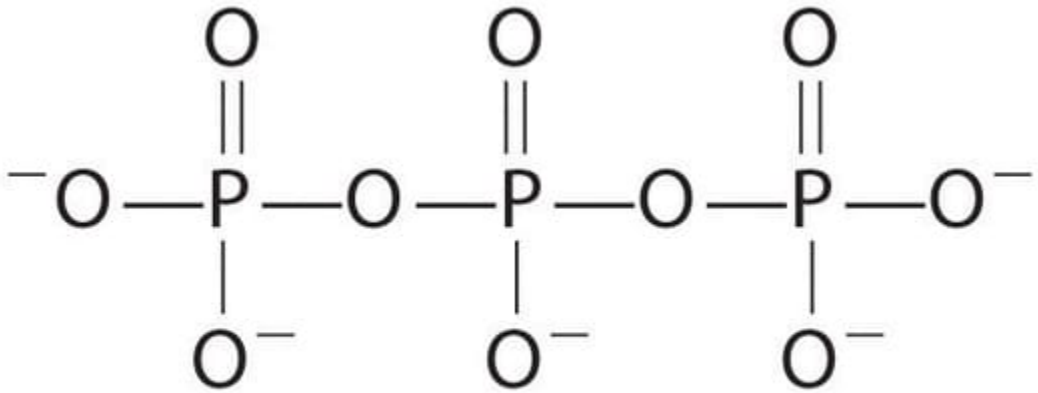
Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

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

$K_{sp} = 2.9 \times 10^{-29}$ for HgI_2 and $K_f = 6.8 \times 10^{29}$ for $[HgI_4]^{2-}$.

Answer a available at the end of this section.

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.



triphosphate

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

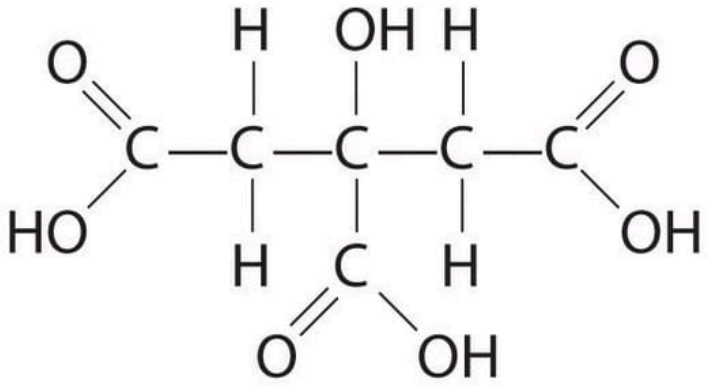
the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:

$$\mathrm{Ca^{2+}\,(aq) + O_3POPO_4^{4-}\,(aq) \rightleftharpoons [Ca(O_3POPO_3)]^{2-}\,(aq)}$$

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.

Complexing Agents in MRIs

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 24.8.2). 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 in Figure 24.8.2.



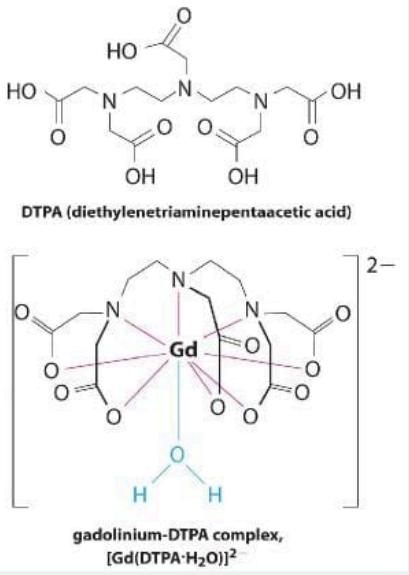


Figure 24.8.2: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Summary

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 24.8.1

2×10^{-6} M

Exercise 24.8.2

1.9×10^{-10} M

1.4 M

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24.9: Acid-Base Reactions of Complex Ions

The pH's of solutions containing hexaaqua ions vary a lot from one metal to another (assuming you are comparing solutions of equal concentrations). However, the underlying explanation is the same for all of them. Consider the hexaaquairon(III) ion, $[Fe(H_2O)_6]^{3+}$ with six water molecules are attached to the central iron(III) ion via a co-ordinate bond using one of the lone pairs on the oxygen. Imagine for the moment that the 3+ charge is located entirely on the iron.

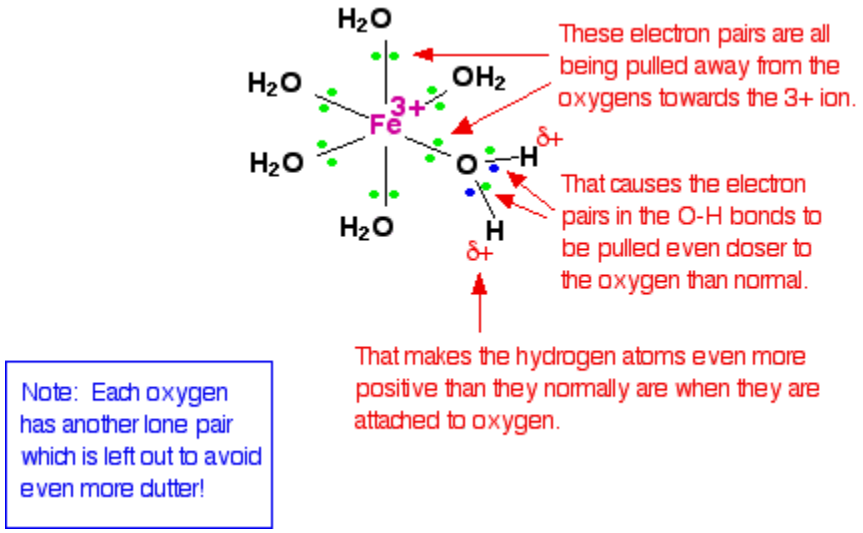


Figure 24.9.1: The hexaaquairon(III) ion, $[Fe(H_2O)_6]^{3+}$, with six water molecules are attached to the central iron(III)

When the lone pairs on the oxygen atoms form co-ordinate bonds with the iron, there is obviously a movement of electrons towards the iron. That has an effect on the electrons in the O-H bonds. These electrons, in turn, get pulled towards the oxygen even more than usual. That leaves the hydrogen nuclei more exposed than normal. The overall effect is that each of the hydrogen atoms is more positive than it is in ordinary water molecules. The 3+ charge is no longer located entirely on the iron, but spreads out over the whole ion - much of it on the hydrogen atoms.

> The 3+ charge is no longer located entirely on the iron, but spreads out over the whole ion - much of it on the hydrogen atoms.

The hydrogen atoms attached to the water ligands are sufficiently positive that they can be pulled off in a reaction involving water molecules in the solution. The first stage of this process is:

$$Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}_{(aq)} + H_3O^+_{(aq)} \tag{24.9.1}$$

The complex ion is acting as an acid by donating a hydrogen ion to water molecules in the solution. The water is, of course, acting as a base by accepting the hydrogen ion. Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify Equation 24.9.1:

$$[Fe(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)} \tag{24.9.2}$$

However, if you write it like this, remember that the hydrogen ion is not just falling off the complex ion. It is being pulled off by a water molecule in the solution. The hexaaquairon(III) ion is q**uite strongly acidic** giving solutions with pH's around 1.5, depending on concentration. You can get further loss of hydrogen ions as well, from a second and a third water molecule.

Losing a second hydrogen ion:

$$[Fe(H_2O)_5(OH)]^{2+}_{(aq)} \rightleftharpoons [Fe(H_2O)_4(OH)_2]^{+}_{(aq)} + H^+_{(aq)} \tag{24.9.3}$$

. . . and a third one:

$$[Fe(H_2O)_4(OH)_2]^+_{(aq)} \rightleftharpoons [Fe(H_2O)_3(OH)_4]_{(s)} + H^+_{(aq)} \tag{24.9.4}$$

This time you end up with a neutral $[Fe(H_2O)_3(OH)_4]_{(s)}$ complex t hat is weakly soluble in water and precipitates.

YouTube Video

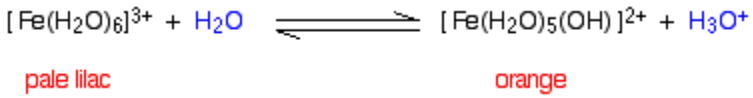
This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 24.9.1***:*** *Combining solutions of sodium hydroxide and iron(III) nitrate produces a precipitate of iron(III) hydroxide. The precipitate can be dissolved by adding a small volume of hydrochloric acid. The precipitate reappears when the sodium hydroxide solution is added again. https://www.youtube.com/watch?v=asdDyWmE9KQ*

Exerimental Perspective

Looking at the equilibrium showing the loss of the first hydrogen ion (Equation 24.9.1):



The color of the new complex ion on the right-hand side is so strong that it completely masks the color of the hexaaqua ion. In concentrated solutions, the equilibrium position will be even further to the right-hand side (Le Chatelier's Principle), and so the color darkens. You will also get significant loss of other hydrogen ions leading to some formation of the neutral complex - and so you get some precipitate. The position of this equilibrium can be shifted by adding extra hydrogen ions from a concentrated acid (e.g., by increasing pH by adding concentrated acid to the solution (Video 24.9.1). The new hydrogen ions push the position of the equilibrium to the left so that you can see the color of the hexaaqua ion:

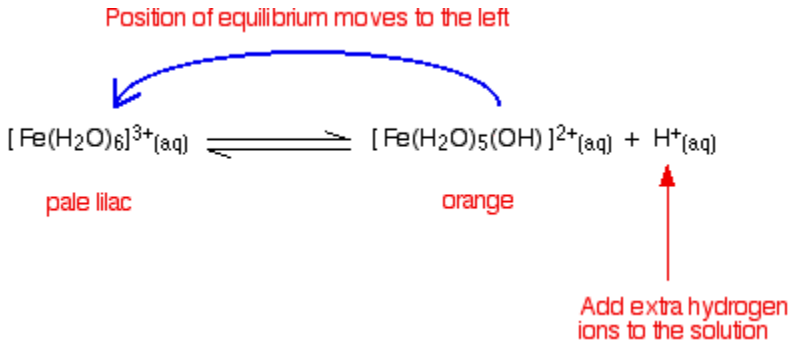


Figure 24.9.2: Le Chatelier's Principle in action for adding acid to $[Fe(H_2O)_6]^{3+}$.

Solutions containing 3+ hexaaqua ions tend to have pH's in the range from 1 to 3. Solutions containing 2+ ions have higher pH's - typically around 5 - 6, although they can go down to about 3. Remember that the reason that these ions are acidic is because of the pull of the electrons towards the positive central ion. An ion with 3+ charges on it is going to pull the electrons more strongly than one with only 2+ charges.

In 3+ ions, the electrons in the O-H bonds will be pulled further away from the hydrogens than in 2+ ions. That means that the hydrogen atoms in the ligand water molecules will have a greater positive charge in a 3+ ion, and so will be more attracted to water molecules in the solution. If they are more attracted, they will be more readily lost - and so the 3+ ions are more acidic.

If you have ions of the same charge, it seems reasonable that the smaller the volume this charge is packed into, the greater the distorting effect on the electrons in the O-H bonds. Ions with the same charge but in a smaller volume (a higher charge density)

would be expected to be more acidic. You would therefore expect to find that the smaller the radius of the metal ion, the stronger the acid. Unfortunately, it's not that simple!

Summary

There probably is a relationship between ionic radius and acid strength, but that it is nothing like as simple and straightforward as most books at this level pretend. The problem is that there are other more important effects operating as well (quite apart from differences in charge) and these can completely swamp the effect of the changes in ionic radius. You have to look in far more detail at the bonding in the hexaaqua ions and the product ions

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24.10: Some Kinetic Considerations

Transition metal complexes which undergo rapid substitution of one ligand for another are **labile**, whereas complexes in which substitution proceed slowly or not at all are **inert**. For an inert complex, it is a large activation energy which prevents ligand substitution. Inert complexes are therefore **kinetically stable** compounds. As a classic example, the substitution reaction:

$$[Co(NH_3)_6]^{3+}_{(aq)} + 6H_3O^+_{(aq)} \rightarrow [Co(H_2O)_6]^{3+}_{(aq)} + 6NH^+_{4(aq)} \tag{24.10.1}$$

has an equilibrium constant of 10^{64}. The large equilibrium constant suggests that the complex ion $[Co(NH_3)_6]^{3+}$ is **thermodynamically unstable**. This reaction is highly thermodynamically favored, yet the inert $[Co(NH_3)_6]^{3+}$ complex ion lasts for weeks in acidic solutions because the rate of the reaction is very slow. Thus, the large activation energy acts as an efficient barrier for ligand substitution rendering the $[Co(NH_3)_6]^{3+}$ ion **thermodynamically metastable**.

The allotropes of carbon

Although diamond is thermodynamically less stable than graphite, diamonds last a long time (~100 million years) since the conversion of diamond into graphite occurs extremely slowly.

Here is an example of a *labile* complex (notice difference in oxidation state for Co in Equation 24.10.1:

$$[Co(NH_3)_6]^{2+}_{(aq)} + 6H_3O^+_{(aq)} \rightarrow [Co(H_2O)_6]^{2+}_{(aq)} + 6NH^+_{4(aq)} \tag{24.10.2}$$

This reaction is virtually complete in a few seconds. The $[Co(NH_3)_6]^{2+}$ complex is thermodynamically unstable and also labile. Notice that the only difference between the two ammine cobalt complexes shown in the examples above is the oxidation number of the cobalt atom. The inert complex has Co(III) while the labile one has Co(II). Both ammine complexes are octahedral and in the case of Co(III), a d^6 species, the t_{2g} levels are filled. Co(II), on the other hand, has partially filled e_g orbitals. It is straightforward to demonstrate lability since changes will occur and ligand substitution in complexes is normally accompanied by a color change. Inertness, however, is somewhat dull since nothing happens. In this experiment the inertness of ligand substitution by chromium (III) ions is compared with other reactions that do proceed at reasonably fast rates.

How to Predict if a Complex is Labile or Inert

Henry Taube (Nobel Prize, 1983) tried to understand lability by comparing the factors that govern bond strengths in ionic complexes to observations about the rates of reaction of coordination complexes. He saw some things that were unsurprising. Taube observed that many M^{+1} ions (M = metal) are more labile than many M^{+3} ions, in general. That is not too surprising, since metal ions function Lewis acids and ligands function Lewis bases in forming coordination complexes. In other words, metals with higher charges ought to be stronger Lewis acids, and so they should bind ligands more tightly. However, there were exceptions to that general rule. For example, Taube also observed that Mo(V) compounds are more labile than Mo(III) compounds. That means there is more going on here than just charge effects. Another factor that governs ionic bond strengths is the size of the ion. Typically, ions with smaller atomic radii form stronger bonds than ions with larger radii. Taube observed that Al^{3+}, V^{3+}, Fe^{3+} and Ga^{3+} ions are all about the same size. All these ions exchange ligands at about the same rate. However, other factors are in play that are outside the scope of this Module.

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

Labile and Inert octahedral Complexes 1. https://www.youtube.com/watch?v=g4fJSM_cE-s

Example 24.10.1

In which compound from each pair would you expect the strongest ionic bonds? Why?

a. LiF vs KBr
b. $CaCl_2$ vs. KCl

Contributors and Attributions

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24.E: Exercises

24.1: Werner's Theory of Coordination Compounds

Conceptual Problems

1. Give two reasons a metal can bind to only a finite number of ligands. Based on this reasoning, what do you predict is the maximum coordination number of Ti? of Ac?
2. Can a tetrahedral MA_2B_2 complex form cis and trans isomers? Explain your answer.
3. The group 12 elements are never found in their native (free) form but always in combination with one other element. What element is this? Why? Which of the group 12 elements has the highest affinity for the element you selected?

Answer

3. The group 12 metals are rather soft and prefer to bind to a soft anion such as sulfide rather than to a hard anion like oxide; hence they are usually found in nature as sulfide ores. Because it is the softest of these metals, mercury has the highest affinity for sulfide.

Structure and Reactivity

1. Complexes of metals in the +6 oxidation state usually contain bonds to which two Lewis bases? Why are these bonds best described as covalent rather than ionic? Do Ca, Sr, and Ba also form covalent bonds with these two Lewis bases, or is their bonding best described as ionic?
2. Cr, Mn, Fe, Co, and Ni form stable CO complexes. In contrast, the earlier transition metals do not form similar stable complexes. Why?
3. The transition metals Cr through Ni form very stable cyanide complexes. Why are these complexes so much more stable than similar compounds formed from the early transition metals?
4. Of $Co(en)_3^{3+}$, CoF_6^{3-}, $Co(NH_3)_6^{3+}$, and $Co(dien)_2^{3+}$, which species do you expect to be the most stable? Why?
5. Of Ca^{2+}, Ti^{2+}, V^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, which divalent metal ions forms the most stable complexes with ligands such as NH_3? Why?
6. Match each Lewis base with the metal ions with which it is most likely to form a stable complex:

   Lewis bases: NH_3, F^-, RS^-, OH^-, and Cl^-

   Metals: Sc^{3+}, Cu^+, W^{6+}, Mg^{2+}, V^{3+}, Fe^{3+}, Zr^{4+}, Co^{2+}, Ti^{4+}, Au^+, Al^{3+}, and Mn^{7+}

7. Of ReF_2, $ReCl_5$, MnF_6, Mn_2O_7, and ReO, which are not likely to exist?
8. Of WF_2, CrF_6, $MoBr_6$, WI_6, CrO_3, MoS_2, W_2S_3, and MoH, which are not likely to exist?

Answers

1. Metals in the +6 oxidation state are stabilized by oxide (O^{2-}) and fluoride (F^-). The M–F and M–O bonds are polar covalent due to extreme polarization of the anions by the highly charged metal. Ca, Sr, and Ba can be oxidized only to the dications (M^{2+}), which form ionic oxides and fluorides.

3. Cyanide is a relatively soft base, and the early transition-metal cations are harder acids than the later transition metals.

5. The formation of complexes between NH_3 and a divalent cation is largely due to electrostatic interactions between the negative end of the ammonia dipole moment and the positively charged cation. Thus the smallest divalent cations (Ni^{2+}, Zn^{2+}, and Cu^{2+}) will form the most stable complexes with ammonia.

7. Re^{2+} is a very soft cation, and F^- and O^{2-} are very hard bases, so ReO and ReF_2 are unlikely to exist. MnF_6 is also unlikely to exist: although fluoride should stabilize high oxidation states, in this case Mn^{6+} is probably too small to accommodate six F^- ions.

24.2: Ligands

Problems

1. Do ligands act like Lewis acids or Lewis bases? Why?
2. Do ligands form ionic bonds with the central metal atom?
3. What are chelating agents?
4. What is a monodentate ligand?
5. Describe polydentate ligands and provide an example.
6. What are hexadentate ligands?

Answers

1. Ligands act like Lewis bases because they share their electron pairs (electron donors) with the central metal atom.
2. No, ligands do not form ionic bonds the with the central metal atom. Rather, they form covalent bonds with the central metal atom because they share electron pairs.
3. Chelating agents are ligands that have two or more atoms with donating electron pairs that are able to attach a metal ion at the same time. These chelating ligands are monodentate and tridentate ligands
4. A monodentate ligand is a ligand that uses only one pair of electrons to bond to the central metal atom or ion.
5. Polydentate ligands are ligands which are able to donate more than two electron pairs to the central metal they bond to. EDTA is an example of a polydentate ligand.
6. Hexadentate ligands are ligands which have six lone pairs of electrons which can all bond to the central metal atom.
7. tetraamminecopper(II) sulfate
8. Tris(ethylenediamine)cobalt(II) nitrate

Problems

Write the name of the following complexes (Chapter 24 / Custom Edition Chapter 21 Exercises):

1. $[CoCl_3(NH_3)_3]$
2. $[Co(ONO)_3(NH_3)_3]$
3. $[Fe(ox)_2(H_2O)_2]^-$
4. $Ag_2[HgI_4]$

Answers

1. triamminetrichlorocobalt(III)
2. triamminetrinitrito-O-cobalt(III); or triamminetrinitritocobalt(III)
3. diaquadioxalatoferrate(III) ion
4. silver(I) tetraiodomercurate(II)

24.3: Nomenclature

24.4: Isomerism

ProblemsEdit section

1. Write the Coordination Isomer for: $[Co(NH_3)_6][Cr(CN)_6]$
2. Write the corresponding linkage isomer as well as names of the two complexes for: $[CoCl(NO_2)(NH_3)_4Cl]$
3. What is the coordination isomer of: $[Cr(NH_3)_6][Fe(CN)_6]$
4. Write the Ionization isomer for: $[CoBr(NH_3)_5]SO_4$
5. Explain a polydentate ligand.

Answers

1. $[Cr(NH_3)_6][Co(CN)_6]$
2. $[CoCl(ONO)(NH_3)_4Cl]$
3. [Fe(NH3)6][Cr(CN)6]
4. $[CoSO_4(NH_3)_5]Br$
5. A polydentate ligand is a ligand that can bind to the central atom of a complex compound at many places at one time.

24.5: Bonding in Complex Ions: Crystal Field Theory

Conceptual Problems

1. Describe crystal field theory in terms of its
   a. assumptions regarding metal–ligand interactions.
   b. weaknesses and strengths compared with valence bond theory.
2. In CFT, what causes degenerate sets of d orbitals to split into different energy levels? What is this splitting called? On what does the magnitude of the splitting depend?
3. Will the value of Δ_o increase or decrease if I^- ligands are replaced by NO_2^- ligands? Why?
4. For an octahedral complex of a metal ion with a d^6 configuration, what factors favor a high-spin configuration versus a low-spin configuration?
5. How can CFT explain the color of a transition-metal complex?

Structure and Reactivity

1. Do strong-field ligands favor a tetrahedral or a square planar structure? Why?
2. For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.
   a. $[TiCl_6]^{3-}$
   b. $[CoCl_4]^{2-}$
3. For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.
   a. $[Cu(NH_3)_4]^{2+}$
   b. $[Ni(CN)_4]^{2-}$
4. The ionic radii of V^{2+}, Fe^{2+}, and Zn^{2+} are all roughly the same (approximately 76 pm). Given their positions in the periodic table, explain why their ionic radii are so similar.

Answers

3.

a. d^9, square planar, neither high nor low spin, single unpaired electron
b. d^8, square planar, low spin, no unpaired electrons

24.6: Magnetic Properties of Coordination Compounds and Crystal Field Theory

24.7: Color and the Colors of Complexes

24.8: Aspects of Complex-Ion Equilibria

Conceptual Problems

1. What is the difference between K_{eq} and K_f?
2. Which would you expect to have the greater tendency to form a complex ion: Mg^{2+} or Ba^{2+}? Why?
3. How can a ligand be used to affect the concentration of hydrated metal ions in solution? How is K_{sp} affected? Explain your answer.
4. Co(II) forms a complex ion with pyridine (C_5H_5N). Which is the Lewis acid, and which is the Lewis base? Use Lewis electron structures to justify your answer.

Numerical Problems

1. Fe(II) forms the complex ion $[Fe(OH)_4]^{2-}$ through equilibrium reactions in which hydroxide replaces water in a stepwise manner. If log K_1 = 5.56, log K_2 = 4.21, log K_3 = −0.10, and log K_4 = −1.09, what is K_f? Write the equilibrium equation that corresponds to each stepwise equilibrium constant. Do you expect the $[Fe(OH)_4]^{2-}$ complex to be stable? Explain your reasoning.
2. Zn(II) forms the complex ion $[Zn(NH_3)_4]^{2+}$ through equilibrium reactions in which ammonia replaces coordinated water molecules in a stepwise manner. If log K_1 = 2.37, log K_2 = 2.44, log K_3 = 2.50, and log K_4 = 2.15, what is the overall K_f? Write the equilibrium equation that corresponds to each stepwise equilibrium constant. Do you expect the $[Zn(NH_3)_4]^{2+}$ complex to be stable? Explain your reasoning.
3. Although thallium has limited commercial applications because it is toxic to humans (10 mg/kg body weight is fatal to children), it is used as a substitute for mercury in industrial switches. The complex ion $[TlBr_6]^{3-}$ is highly stable, with log K_f = 31.6. What is the concentration of Tl(III)(aq) in equilibrium with a 1.12 M solution of $Na_3[TlBr_6]$?

Answer

1.

$$[Fe(H_2O)_6]^{2+}(aq) + OH^-(aq) \diamondsuit [Fe(H_2O(aq))_5(OH)] + (aq) + H_2O \log K_1 = 5.56$$
$$[Fe(H_2O)_5(OH)] + (aq) + OH^-(aq) \diamondsuit [Fe(H_2O)_4(OH)_2](aq) + H_2O(aq) \log K_2 = 9.77$$
$$[Fe(H_2O)_4(OH)_2](aq) + OH^-(aq) \diamondsuit [Fe(H_2O)_3(OH)_3]^-(aq) + H_2O(aq) \log K_3 = 9.67$$
$$[Fe(H_2O)_3(OH)_3]^-(aq) + OH^-(aq) \diamondsuit [Fe(OH)_4]^{2-}(aq) + 3H_2O(l) \log K_4 = 8.58$$
$$[Fe(H_2O)_6]^{2+}(aq) + 4OH^-(aq) \diamondsuit [Fe(OH)_4]^{2-}(aq) + 6H_2O(l)$$
$$\log K_f = \log K_1 + \log K_2 + \log K_2 + \log K_4$$
$$= 33.58$$

Thus, $K_f = 3.8 \times 10^{33}$. Because $[Fe(OH)_4]^{2-}$ has a very large value of K_f, it should be stable in the presence of excess OH^-.

24.9: Acid-Base Reactions of Complex Ions

24.10: Some Kinetic Considerations

24.11: Applications of Coordination Chemistry

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25: NUCLEAR CHEMISTRY

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

- Topic hierarchy

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25.1: 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:

$$^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X} \tag{25.1.1}$$

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 $25.1.1$ shows how we can identify a nuclide by balancing the

nuclear reaction.

Example 25.1.1: 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 25.1.1

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 25.1.1 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 25.1.1: 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 25.1.1. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.

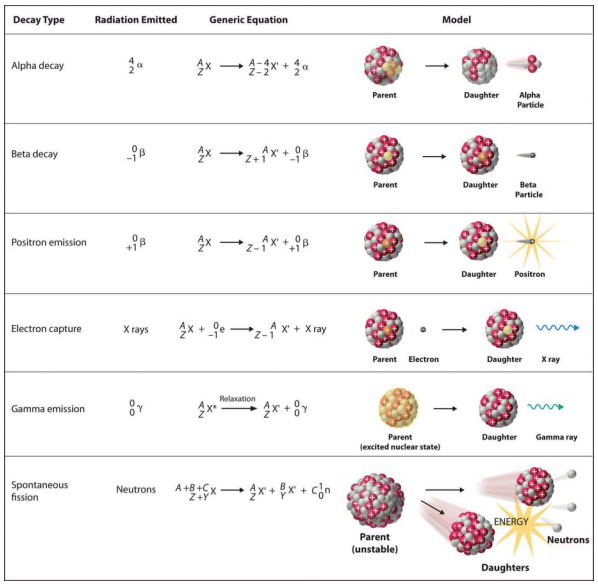


Figure 25.1.1: Common Modes of Nuclear Decay

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:

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A-4}_{Z-2}\text{X}'} + \underset{\substack{\text{alpha}\\\text{particle}}}{{}^{4}_{2}\alpha} \tag{25.1.2}$$

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:

$${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha \tag{25.1.3}$$

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:

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^{0}_{-1}\beta} \tag{25.1.4}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{25.1.5}$$

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:

$$^{1}_{1}\mathrm{p}^{+} \rightarrow ^{1}_{0}\mathrm{n} + ^{0}_{+1}\beta^{+} \tag{25.1.6}$$

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:

$$^{1}_{1}\mathrm{p} + ^{0}_{-1}\mathrm{e} \rightarrow ^{1}_{0}\mathrm{n} \tag{25.1.7}$$

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 25.1.2

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 25.1.2

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 25.1.3

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 25.1.3

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 25.1.2). 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.

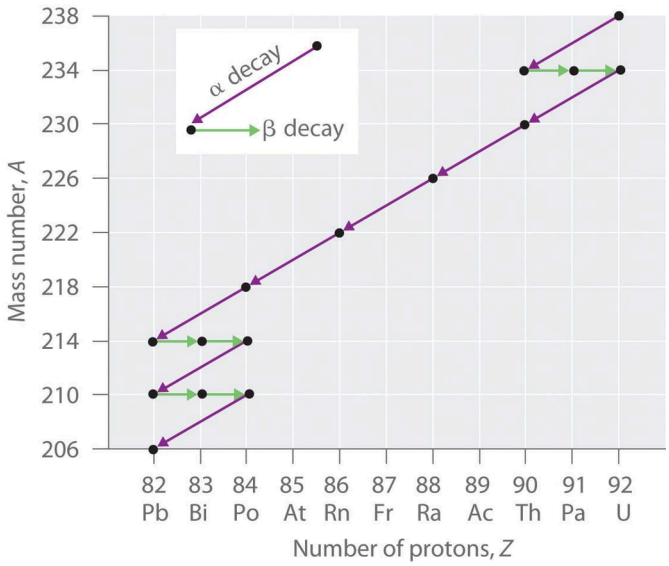


Figure 25.1.2 A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

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:

$$ {}^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{25.1.8} $$

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 25.1.3). 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:

$$ {}^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{25.1.9} $$

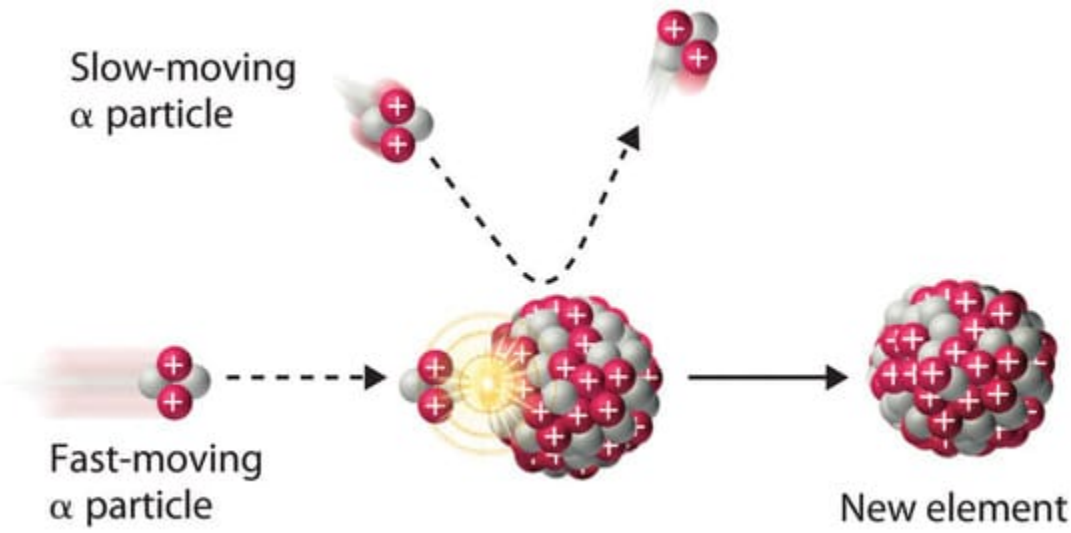


Figure 25.1.3: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively 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 25.1.4

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 25.1.4

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 25.1.4:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{25.1.10}$$

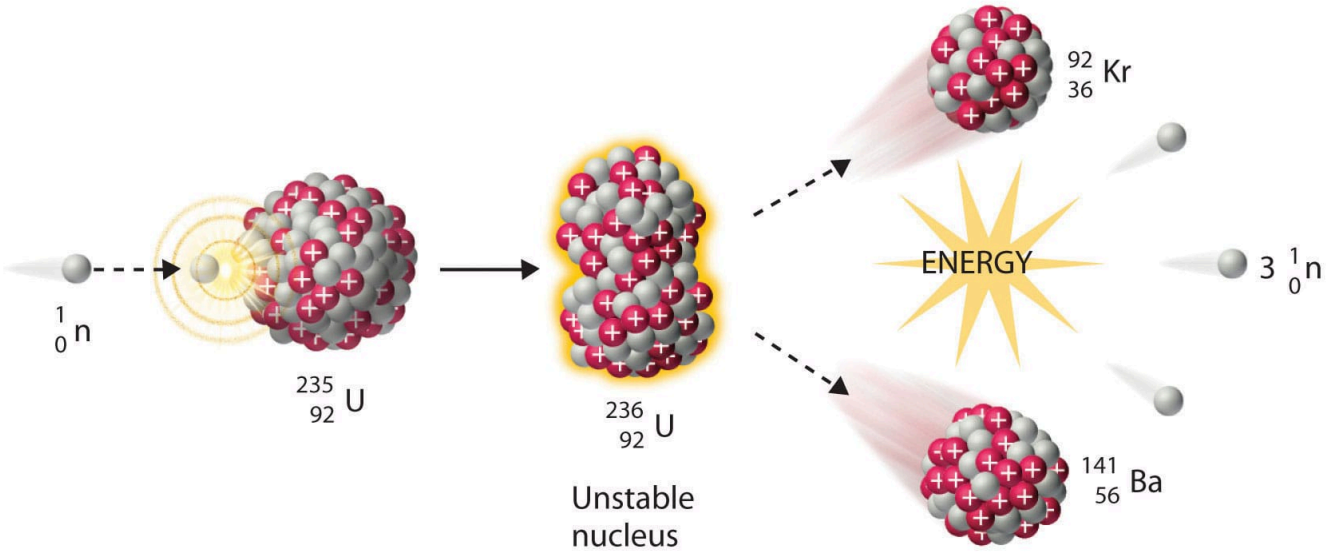


Figure 25.1.4 Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

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 25.1.4. 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 25.1.5, 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.

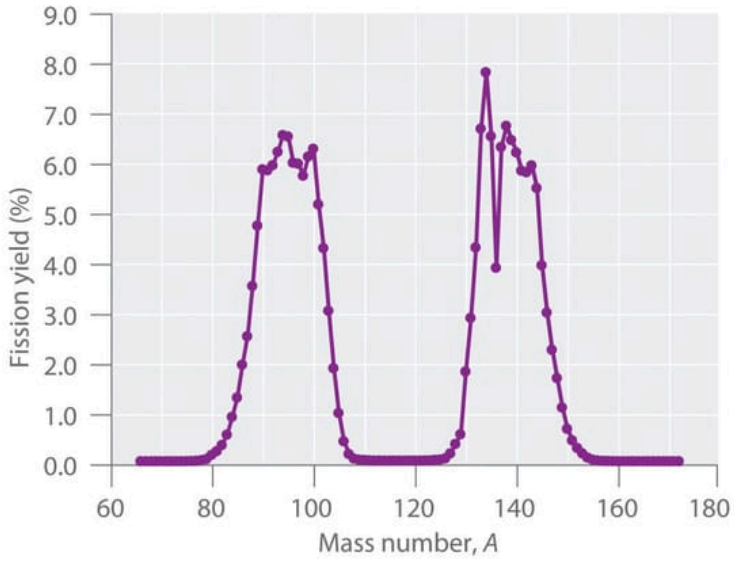


Figure 25.1.5: Mass Distribution of Nuclear Fission Products of ^{235}U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different 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 25.1.2). 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 25.1.2: 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 25.1.6), 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.

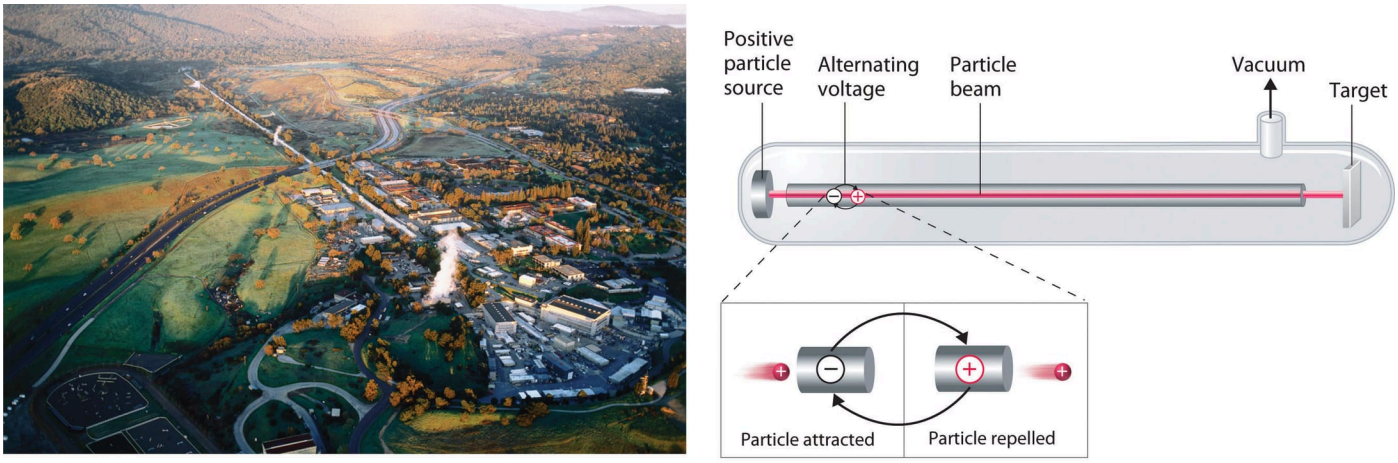


Figure 25.1.6: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as 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 25.1.1

$$ {}^{125}_{53}\mathrm{I} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{125}_{52}\mathrm{Te} $$

Exercise 25.1.2

$ {}^{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 25.1.3

beta decay

positron emission or electron capture

alpha decay

Exercise 25.1.4

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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25.2: Naturally Occurring Radioactive Isotopes

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 25.2.1. 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 25.2.1 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 25.2.1 for some common elements.

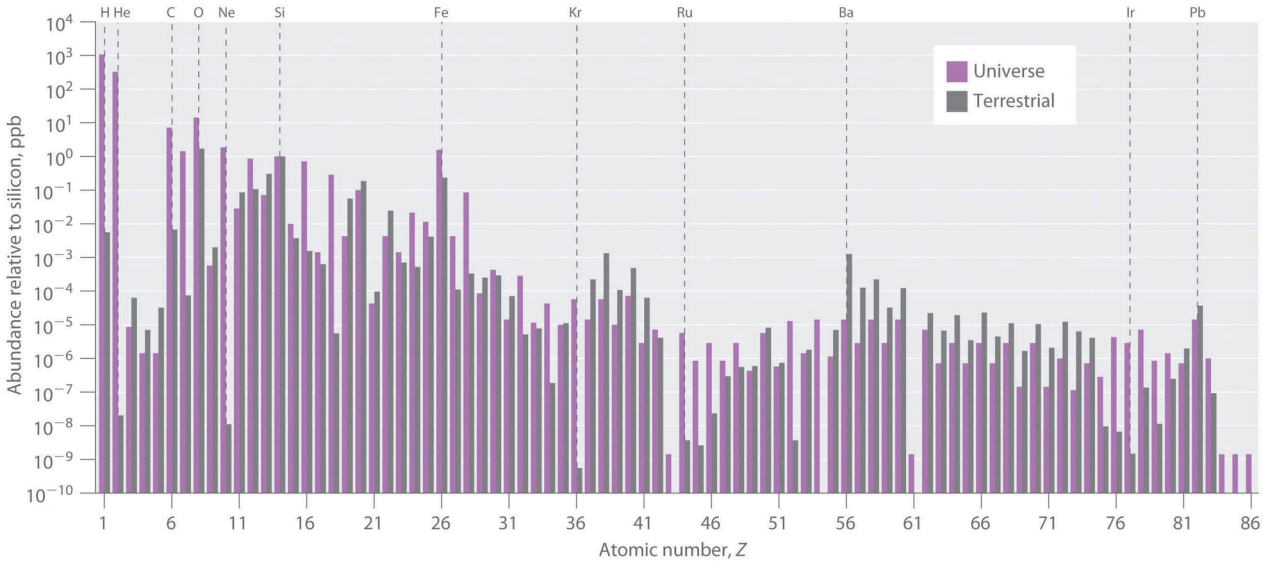


Figure 25.2.1: The Relative Abundances of the Elements in the Universe and on Earth. In this logarithmic plot, the relative abundances of the elements relative to that of silicon (arbitrarily set equal to 1) in the universe (green bars) and on Earth (purple bars) are shown as a function of atomic number. 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.

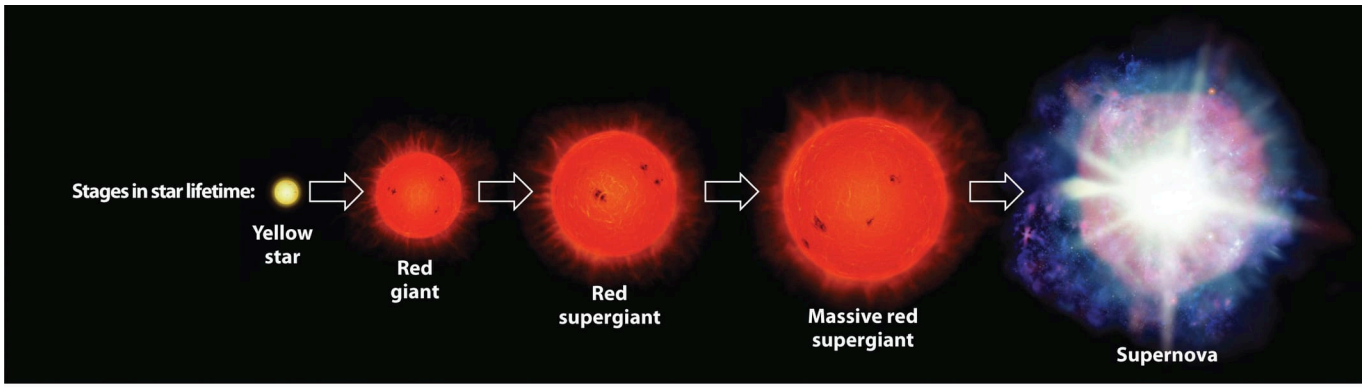
Table 25.2.1: Relative Abundances of Elements on Earth and in the Known Universe

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 25.2.2). 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 25.2.2: 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:

$$\begin{aligned} {}^1_1\text{H} + {}^1_1\text{H} &\rightarrow {}^2_1\text{H} + {}^0_{+1}\beta \\ {}^2_1\text{H} + {}^1_1\text{H} &\rightarrow {}^3_2\text{He} + {}^0_0\gamma \\ {}^3_2\text{He} + {}^3_2\text{He} &\rightarrow {}^4_2\text{He} + 2{}^1_1\text{H} \end{aligned} \tag{25.2.1}$$

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:

$$4{}^1_1\text{H} \rightarrow {}^4_2\text{He} + 2{}^0_{+1}\beta + 2{}^0_0\gamma \tag{25.2.2}$$

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:

$$2{}^4_2\text{He} \rightarrow {}^8_4\text{Be} \tag{25.2.3}$$

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:

$${}^8_4\text{Be} \xrightarrow{{}^4_2\text{He}} {}^{12}_6\text{C} \xrightarrow{{}^4_2\text{He}} {}^{16}_8\text{O} \xrightarrow{{}^4_2\text{He}} {}^{20}_{10}\text{Ne} \xrightarrow{{}^4_2\text{He}} {}^{24}_{12}\text{Mg} \tag{25.2.4}$$

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:

$$^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{23}_{11}\mathrm{Na} + {}^{1}_{1}\mathrm{H} \tag{25.2.5}$$

$$^{12}_{6}\mathrm{C} + {}^{16}_{8}\mathrm{O} \rightarrow {}^{28}_{14}\mathrm{Si} + {}^{0}_{0}\gamma \tag{25.2.6}$$

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:

$$^{12}_{6}\mathrm{C} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{16}_{8}\mathrm{O} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{20}_{10}\mathrm{Ne} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{24}_{12}\mathrm{Mg} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{28}_{14}\mathrm{Si} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{32}_{16}\mathrm{S} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{36}_{18}\mathrm{Ar} \xrightarrow{^{4}_{2}\mathrm{He}} {}^{40}_{20}\mathrm{Ca} \tag{25.2.7}$$

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 25.2.2). 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 25.2.3). 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:

$$^{56}_{26}\mathrm{Fe} + 64\,^{1}_{0}\mathrm{n} \rightarrow {}^{120}_{26}\mathrm{Fe} \rightarrow {}^{120}_{50}\mathrm{Sn} + 24\,^{0}_{-1}\beta \tag{25.2.8}$$



Figure 25.2.3: 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 25.2.1: 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 25.2.1

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 25.2.1

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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25.3: Nuclear Reactions and Artificially Induced Radioactivity

Radioactivity is the process by which the nucleus of an unstable atom loses energy by emitting radiation, including alpha particles, beta particles, gamma rays and conversion electrons Although radioactivity is observed as a natural occurring process, it can also be artificially induced typically via the bombarding atoms of a specific element by radiating particles, thus creating new atoms.

Introduction

Ernest Rutherford was a prominent New Zealand scientist, and a winner of the Nobel Prize in chemistry in 1908. Amongst his vast list of discoveries, Rutherford was also the first to discover artificially induced radioactivity. Through the bombardment of alpha particles against nuclei of $^{14}\mathrm{N}$ with 7 protons/electrons, Rutherford produced $^{17}\mathrm{O}$ (8 protons/electrons) and protons (Figure $25.3.1$). Through this observation, Rutherford concluded that atoms of one specific element can be made into atoms of another element. If the resulting element is radioactive, then this process is called **artificially induced radioactivity**

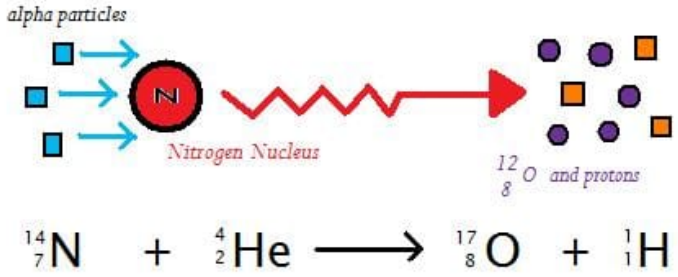


Figure $25.3.1$: Rutherford generated $^{17}\mathrm{O}$ *via bombarding* $^{14}\mathrm{N}$ *with alpha particles.*

Rutherford was the first researcher to create protons outside of the atomic nuclei and the $^{17}\mathrm{O}$ isotope of oxygen, which is nonradioactive. Similarly, other nuclei when bombarded with alpha particles will generate new elements (Figure $25.3.2$) that may be radioactive and decay naturally or that may be stable and persist like $^{17}\mathrm{O}$.

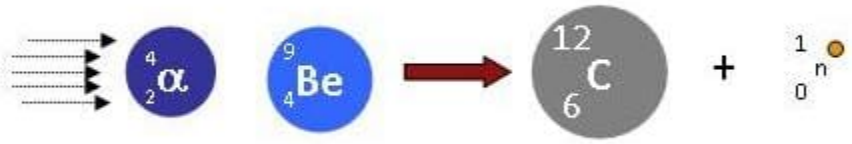


Figure $25.3.2$: Researchers have used α particle to react with another atom such as Beryllium. The result is a Carbon nucleus and a neutron. This is artificial radioactivity or induced radioactivity. from igem.org.

Before this discovery of artificial induction of radioactivity, it was a common belief that atoms of matter are unchangeable and indivisible. After the very first discoveries made by Ernest Rutherford, Irene Joliot-Curie and her husband, Frederic Joliot, a new point of view was developed. The point of view that although atoms appear to be stable, they can be transformed into new atoms with different chemical properties. Today over one thousand artificially created radioactive nuclides exist, which considerably outnumber the nonradioactive ones created.

Note: Irene Joliet-Curie and Frederic Joliot

Irene Joliet-Curie and her husband Frédéric both were French scientists who shared winning the Nobel Prize award in chemistry in 1935 for artificially synthesizing a radioactive isotope of phosphorus by bombarding aluminum with alpha particles. $^{30}\mathrm{P}$ with 15 protons was the first radioactive nuclide obtained through this method of artificially inducing radioactivity.

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n} \tag{25.3.1}$$

$$^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{-1}\beta \tag{25.3.2}$$



Figure 25.3.3: *Researchers can use neutrons to react with atoms (for example 235 Uranium) to generate a bigger nuclei with an excess of neutron leading to an increase of the unstability and the new nucleus can split into two smaller nuclei. This phenomenon is the sometimes called neutronic fission. from igem.org.*

Activation (or radioactivation) involves making a radioactive isotope by neutron capture, e.g. the addition of a neutron to a nuclide resulting in an increase in isotope number by 1 while retaining the same atomic number (Figure 25.3.3). Activation is often an inadvertent process occurring inside or near a nuclear reactor, where there are many neutrons flying around. For example, Coba in or near a nuclear reactor will capture a neutron forming the radioactive isotope Co-60.

$$^{1}_{0}\mathrm{n} + {}^{59}\mathrm{Co} \rightarrow {}^{60}\mathrm{Co} \tag{25.3.3}$$

The $^{60}\mathrm{Co}$ isotope is unstable (half life of 5.272 years) and disintegrates into $^{60}\mathrm{Ni}$ via the emission of β particle and γ radiation Figure 25.3.4.

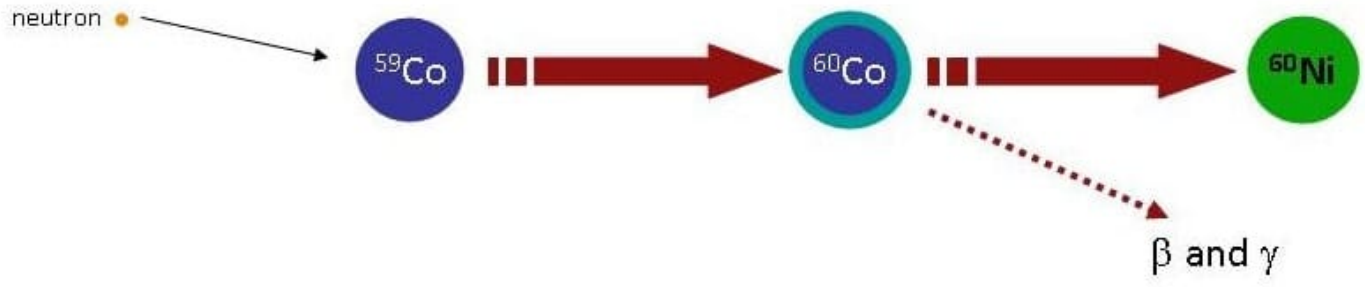


Figure 25.3.4: Example of $^{59}\mathrm{Co}$ activation and $^{60}\mathrm{Co}$ disintegration. *from igem.org.*

Example 25.3.1: Neutron Bombardment

Write a nuclear equation for the creation of ^{56}Mn through the bombardment of ^{59}Co with neutrons.

Solution

A unknown particle is produced with ^{56}Mn, in order to find the mass number (A) of the unknown we must subtract the mass number of the Manganese atom from the mass number of the Cobalt atom plus the neutron being thrown. In simpler terms,



Now, by referring to a periodic table to find the atomic numbers of Mn and Co, and then subtracting the atomic number of Mn from Co, we will receive the atomic number of the unknown particle



Thus, the unknown particle has A = 4, and Z = 2, which would make it a Helium particle, and the nuclear formula would be as follows:

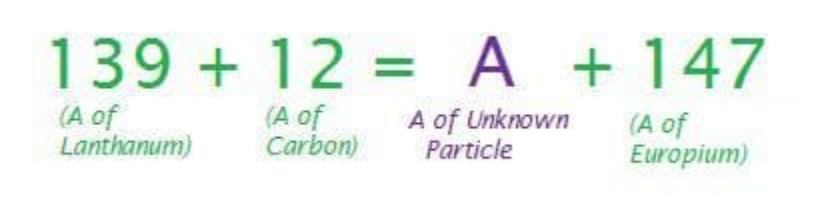
$$^{50}_{27}\mathrm{Co} + ^{1}_{0}\mathrm{n} \rightarrow ^{56}_{25}\mathrm{Mn} + ^{4}_{2}\alpha$$

Example 25.3.2: Calcium Bombardment

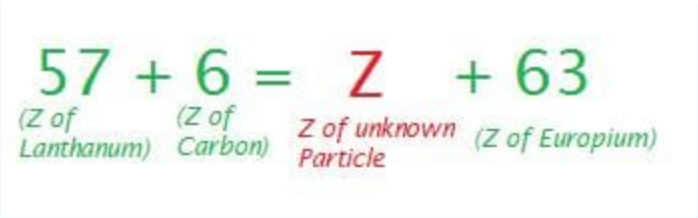
Write a nuclear equation for the production of $^{147}\mathrm{Eu}$ by bombardment of $^{139}\mathrm{La}$ with $^{12}\mathrm{Ca}$.

Solution

Like the above example, you must first find the mass number of the unknown particle.



Thus, the mass number of the unknown particle is 4. Again by referring to a periodic table and finding the atomic numbers of Lanthanum, Carbon and Europium, we are able to calculate the atomic number of the unknown particle,



The atomic number for the unknown particle equals to zero, therefore 4 neutrons are emitted, and the nuclear equation is written as follows:

$$^{139}_{57}\mathrm{La} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{147}_{63}\mathrm{Eu} + 4\,{}^{0}_{1}\mathrm{n}$$

Summary

Induced radioactivity occurs when a previously stable material has been made radioactive by exposure to specific radiation. Most radioactivity does not induce other material to become radioactive. This Induced radioactivity was discovered by Irène Curie and F. Joliot in 1934. This is also known as man-made radioactivity. The phenomenon by which even light elements are made radioactive by artificial or induced methods is called artificial radioactivity.

References

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2. Savel, Pierre. "Atomic Energy." The Discovery of Artificial Radioactivity Vol.16 No.6 (1964), pp. 534-537

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25.4: 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:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta \tag{25.4.1}$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta \tag{25.4.2}$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 25.4.1). 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." As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval.

Table 25.4.1: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{240}_{95}\mathrm{Am} + {}^{0}_{-1}\mathrm{e}$
curium	Cm	96	$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
californium	Cf	98	$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{243}_{97}\mathrm{Bk} + 2{}^{1}_{0}\mathrm{n}$
einsteinium	Es	99	$^{238}_{92}\mathrm{U} + 15{}^{1}_{0}\mathrm{n} \longrightarrow {}^{253}_{99}\mathrm{Es} + 7{}^{0}_{-1}\mathrm{e}$
mendelevium	Md	101	$^{253}_{99}\mathrm{Es} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$
nobelium	No	102	$^{246}_{96}\mathrm{Cm} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{254}_{102}\mathrm{No} + 4\,{}^{1}_{0}\mathrm{n}$
rutherfordium	Rf	104	$^{249}_{98}\mathrm{Cf} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{257}_{104}\mathrm{Rf} + 4\,{}^{1}_{0}\mathrm{n}$
seaborgium	Sg	106	$^{206}_{82}\mathrm{Pb} + {}^{54}_{24}\mathrm{Cr} \longrightarrow {}^{257}_{106}\mathrm{Sg} + 3\,{}^{1}_{0}\mathrm{n}$ $^{249}_{98}\mathrm{Cf} + {}^{18}_{8}\mathrm{O} \longrightarrow {}^{263}_{106}\mathrm{Sg} + 4\,{}^{1}_{0}\mathrm{n}$
meitnerium	Mt	107	$^{209}_{83}\mathrm{Bi} + {}^{58}_{26}\mathrm{Fe} \longrightarrow {}^{266}_{109}\mathrm{Mt} + {}^{1}_{0}\mathrm{n}$

Particle Accelerators

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 25.4.2), 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.

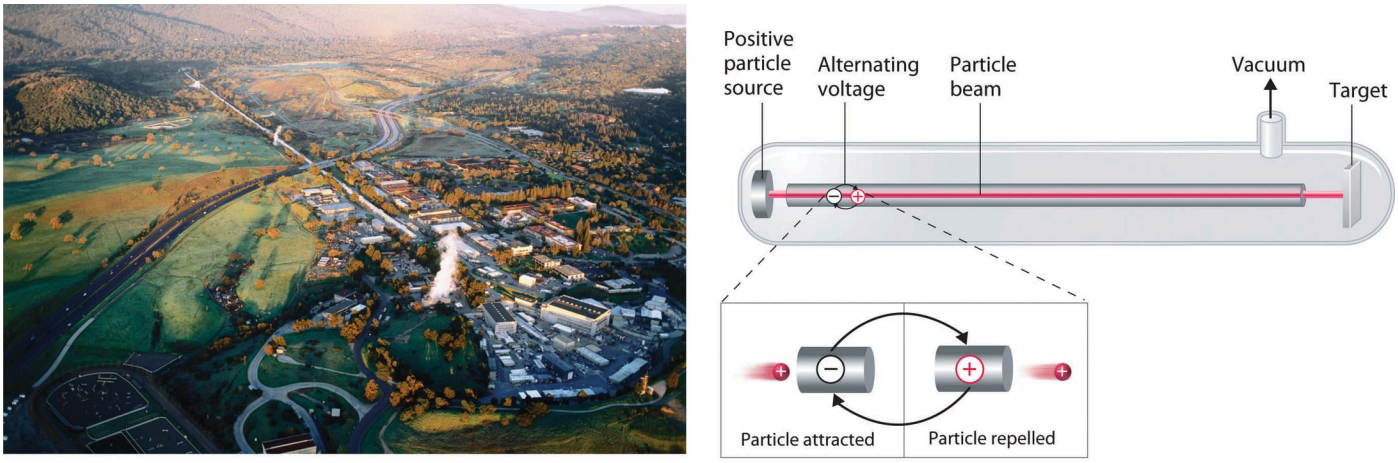


Figure 25.4.2: *A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as 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.

Contributors and Attributions

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25.5: Rate of Radioactive Decay

Learning Objectives

- Recognize common modes of radioactive decay
- Identify common particles and energies involved in nuclear decay reactions
- Write and balance nuclear decay equations
- Calculate kinetic parameters for decay processes, including half-life
- Describe common radiometric dating techniques

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term "radioactivity," and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is radioactive decay. The unstable nuclide is called the parent nuclide; the nuclide that results from the decay is known as the daughter nuclide. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo (Figure 25.5.1).

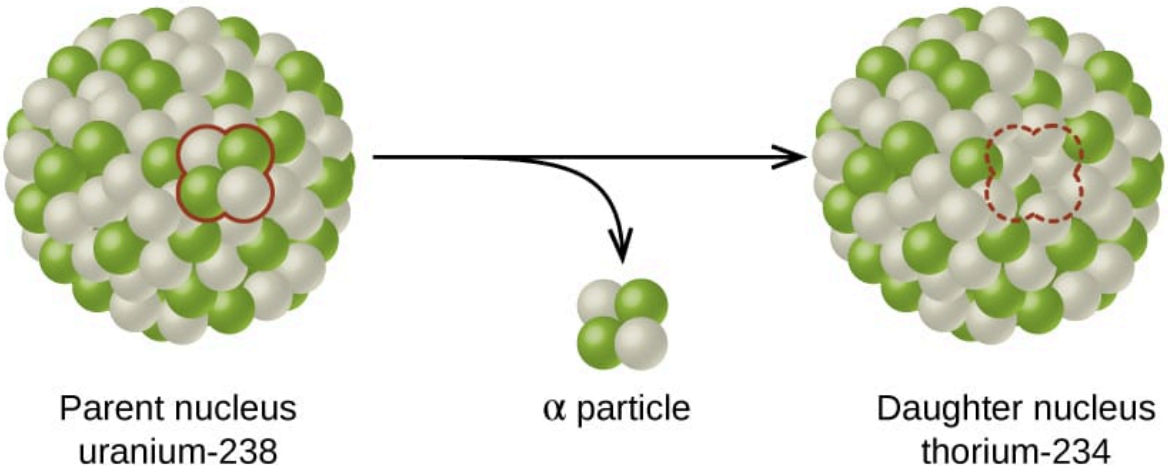


Figure 25.5.1: A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.

A diagram shows two spheres composed of many smaller white and green spheres connected by a right-facing arrow with another, down-facing arrow coming off of it. The left sphere, labeled "Parent nucleus uranium dash 238" has two white and two green spheres that are near one another and are outlined in red. These two green and two white spheres are shown near the tip of the down-facing arrow and labeled "alpha particle." The right sphere, labeled "Daughter nucleus radon dash 234," looks the same as the left, but has a space for four smaller spheres outlined with a red dotted line.

Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Click here to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.

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 25.5.1: How to Build a Cloud Chamber!

Types of Radioactive Decay

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field (Figure 25.5.2) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, γ rays. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

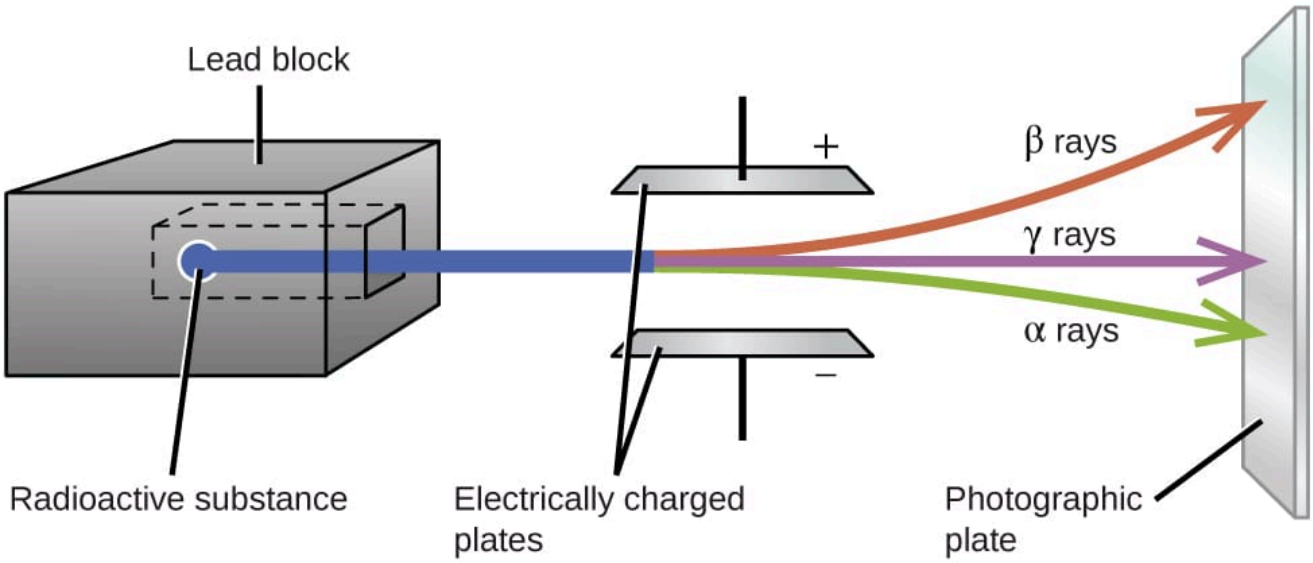


Figure 25.5.2: Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

A diagram is shown. A gray box on the left side of the diagram labeled "Lead block" has a chamber hollowed out in the center in which a sample labeled "Radioactive substance" is placed. A blue beam is coming from the sample, out of the block, and passing through two horizontally placed plates that are labeled "Electrically charged plates." The top plate is labeled with a positive sign while the bottom plate is labeled with a negative sign. The beam is shown to break into three beams as it passes in between the plates; in order from top to bottom, they are red, labeled "beta rays," purple labeled "gamma rays" and green labeled "alpha rays." The beams are shown to hit a vertical plate labeled "Photographic plate" on the far right side of the diagram.

Alpha (α) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:

$$^{210}_{84}\mathrm{Po} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{206}_{82}\mathrm{Pb} \qquad ^{210}_{84}\mathrm{Po} \longrightarrow {}^{4}_{2}\alpha + {}^{206}_{82}\mathrm{Pb}$$

Alpha decay occurs primarily in heavy nuclei (A > 200, Z > 83). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below **the band of stability**, the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:

$$^{131}_{53}\mathrm{I} \longrightarrow {}^{0}_{-1}\mathrm{e} + {}^{131}_{54}\mathrm{X} \qquad\qquad ^{131}_{53}\mathrm{I} \longrightarrow {}^{0}_{-1}\beta + {}^{131}_{54}\mathrm{Xe}$$

Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:

$$^{60}_{27}\mathrm{Co}^{*} \longrightarrow {}^{0}_{0}\gamma + {}^{60}_{27}\mathrm{Co}$$

There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β^{+} decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:

$$^{15}_{8}\mathrm{O} \longrightarrow {}^{0}_{+1}\mathrm{e} + {}^{15}_{7}\mathrm{N} \qquad\qquad ^{15}_{8}\mathrm{O} \longrightarrow {}^{0}_{+1}\beta + {}^{15}_{7}\mathrm{N}$$

Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:

$$^{40}_{19}\mathrm{K} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{40}_{18}\mathrm{Ar}$$

Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur. Figure $25.5.3$ summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

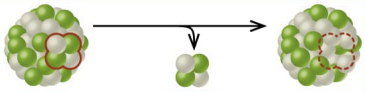
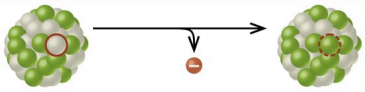
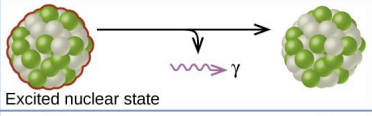
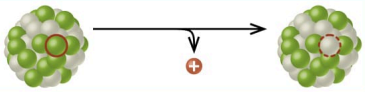
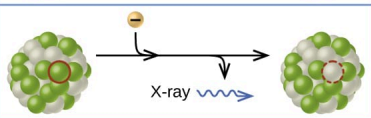
Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}X \rightarrow {}^{4}_{2}He + {}^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Z+1}Y$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}X \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}Y$		A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}X \rightarrow {}^{0}_{+1}e + {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1

Figure 25.5.3: This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

This table has four columns and six rows. The first row is a header row and it labels each column: “Type,” “Nuclear equation,” “Representation,” and “Change in mass / atomic numbers.” Under the “Type” column are the following: “Alpha decay,” “Beta decay,” “Gamma decay,” “Positron emission,” and “Electron capture.” Under the “Nuclear equation” column are several equations. Each begins with superscript A stacked over subscript Z X. There is a large gap of space and then the following equations: “superscript 4 stacked over subscript 2 He plus superscript A minus 4 stacked over subscript Z minus 2 Y,” “superscript 0 stacked over subscript negative 1 e plus superscript A stacked over subscript Z plus 1 Y,” “superscript 0 stacked over subscript 0 lowercase gamma plus superscript A stacked over subscript Z Y,” “superscript 0 stacked over subscript positive 1 e plus superscript A stacked over subscript Y minus 1 Y,” and “superscript 0 stacked over subscript negative 1 e plus superscript A stacked over subscript Y minus 1 Y.” Under the “Representation” column are the five diagrams. The first shows a cluster of green and white spheres. A section of the cluster containing two white and two green spheres is outlined. There is a right-facing arrow pointing to a similar cluster as previously described, but the outlined section is missing. From the arrow another arrow branches off and points downward. The small cluster to two white spheres and two green spheres appear at the end of the arrow. The next diagram shows the same cluster of white and green spheres. One white sphere is outlined. There is a right-facing arrow to a similar cluster, but the white sphere is missing. Another arrow branches off the main arrow and a red sphere with a negative sign appears at the end. The next diagram shows the same cluster of white and green spheres. The whole sphere is outlined and labeled, “excited nuclear state.” There is a right-facing arrow that points to the same cluster. No spheres are missing. Off the main arrow is another arrow which points to a purple squiggle arrow which in turn points to a lowercase gamma. The next diagram shows the same cluster of white and green spheres. One green sphere is outlined. There is a right-facing arrow to a similar cluster, but the green sphere is missing. Another arrow branches off the main arrow and a red sphere with a positive sign appears at the end. The next diagram shows the same cluster of white and green spheres. One green sphere is outlined. There is a right-facing arrow to a similar cluster, but the green sphere is missing. Two other arrows branch off the main arrow. The first shows a gold sphere with a negative sign joining with the right-facing arrow. The secon points to a blue squiggle arrow labeled, “X-ray.” Under the “Change in mass / atomic numbers” column are the following: “A: decrease by 4, Z: decrease by 2,” “A: unchanged, Z: increased by 1,” “A: unchanged, Z: unchanged,” “A: unchanged, Z: unchanged,” “A: unchanged, Z: decrease by 1,” and “A: unchanged, Z: decrease by 1.”

PET Scan

Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how parts of a patient’s body function (Figure 25.5.4). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This “tagged” compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.

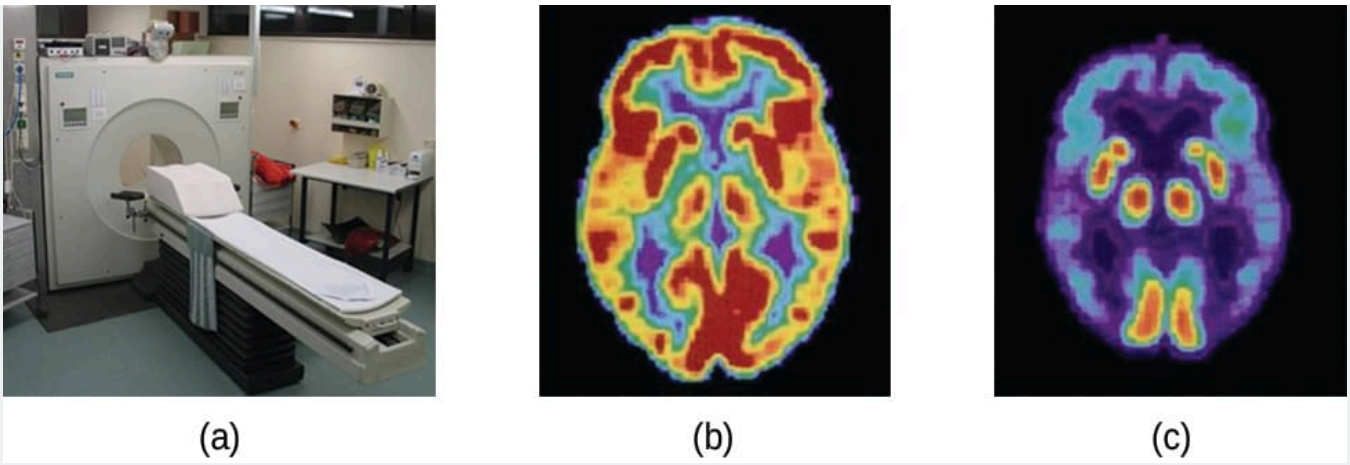


Figure 25.5.4: A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)

Three pictures are shown and labeled "a," "b" and "c." Picture a shows a machine with a round opening connected to an examination table. Picture b is a medical scan of the top of a person's head and shows large patches of yellow and red and smaller patches of blue, green and purple highlighting. Picture c also shows a medical scan of the top of a person's head, but this image is mostly colored in blue and purple with very small patches of red and yellow.

For example, F-18 is produced by proton bombardment of ^{18}O ($^{18}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p} \longrightarrow {}^{18}_{9}\mathrm{F} + {}^{1}_{0}\mathrm{n}$) and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The ^{18}F emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or radioactive decay series. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (Figure 25.5.5). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.

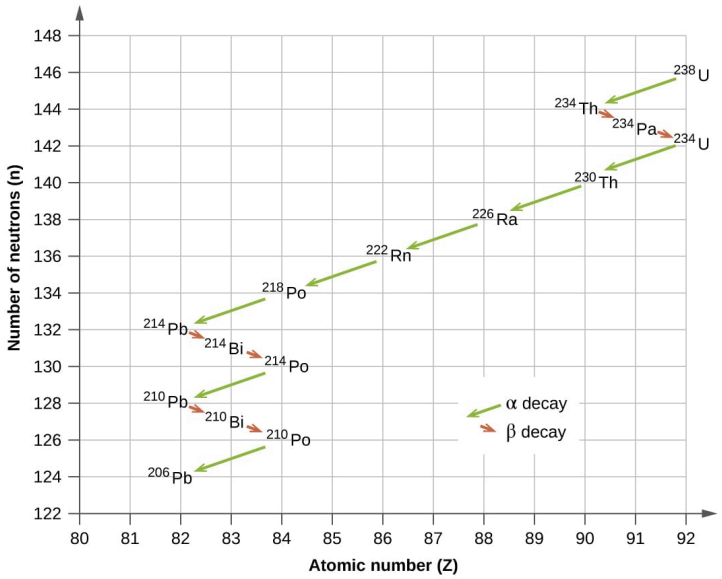


Figure 25.5.5: Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

A graph is shown where the x-axis is labeled “Number of neutrons, open parenthesis, n, close parenthesis” and has values of 122 to 148 in increments of 2. The y-axis is labeled “Atomic number” and has values of 80 to 92 in increments of 1. Two types of arrows are used in this graph to connect the points. Green arrows are labeled as “alpha decay” while red arrows are labeled “beta decay.” Beginning at the point “92, 146” that is labeled “superscript 238, U,” a green arrow connects this point to the second point “90, 144” which is labeled “superscript 234, T h.” A red arrow connect this to the third point “91, 143” which is labeled “superscript 234, P a” which is connected to the fourth point “92, 142” by a red arrow and which is labeled “superscript 234, U.” A green arrow leads to the next point, “90, 140” which is labeled “superscript 230, T h” and is connected by a green arrow to the sixth point, “88, 138” which is labeled “superscript 226, R a” that is in turn connected by a green arrow to the seventh point “86, 136” which is labeled “superscript 222, Ra.” The eighth point, at “84, 134” is labeled “superscript 218, P o” and has green arrows leading to it and away from it to the ninth point “82, 132” which is labeled “superscript 214, Pb” which is connected by a red arrow to the tenth point, “83, 131” which is labeled “superscript 214, B i.” A red arrow leads to the eleventh point “84, 130” which is labeled “superscript 214, P o” and a green arrow leads to the twelvth point “82, 128” which is labeled “superscript 210, P b.” A red arrow leads to the thirteenth point “83, 127” which is labeled “superscript 210, B i” and a red arrow leads to the fourteenth point “84, 126” which is labeled “superscript 210, P o.” The final point is labeled “82, 124” and “superscript 206, P b.”

Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant half-life ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope’s half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years (Figure 25.5.6). In a given cobalt-60 source, since half of the $^{60}_{27}\mathrm{Co}$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

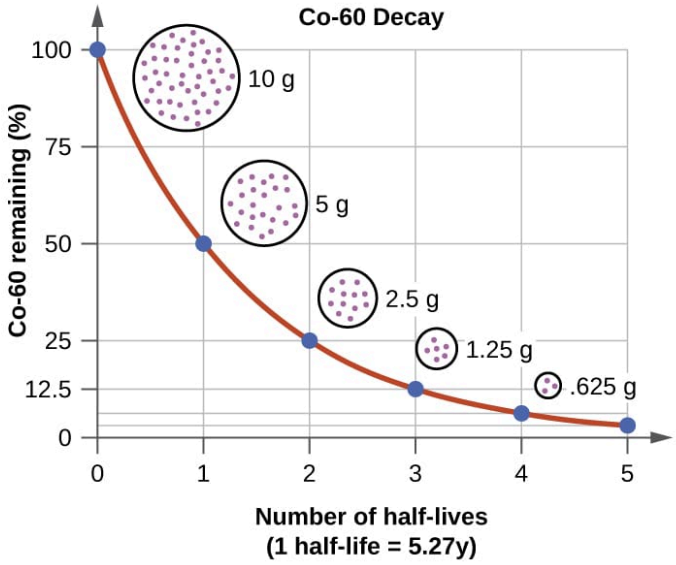


Figure 25.5.6: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

A graph, titled “C o dash 60 Decay,” is shown where the x-axis is labeled “C o dash 60 remaining, open parenthesis, percent sign, close parenthesis” and has values of 0 to 100 in increments of 25. The y-axis is labeled “Number of half dash lives” and has values of 0 to 5 in increments of 1. The first point, at “0, 100” has a circle filled with tiny dots drawn near it labeled “10 g.” The second point, at “1, 50” has a smaller circle filled with tiny dots drawn near it labeled “5 g.” The third point, at “2, 25” has a small circle filled with tiny dots drawn near it labeled “2.5 g.” The fourth point, at “3, 12.5” has a very small circle filled with tiny dots drawn near it labeled “1.25 g.” The last point, at “4, 6.35” has a tiny circle filled with tiny dots drawn near it labeled.”625 g.”

Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions. We generally substitute the number of nuclei, *N*, for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the activity of the radioactive sample. The rate for radioactive decay is:

$$\text{decay rate} = \lambda N$$

with λ is the **decay constant** for the particular radioisotope.

The decay constant, λ, which is the same as a rate constant discussed in the kinetics chapter. It is possible to express the decay constant in terms of the half-life, $t_{1/2}$:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \qquad \text{or} \qquad t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

The first-order equations relating amount, *N*, and time are:

$$N_t = N_0 e^{-kt} \qquad \text{or} \qquad t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right)$$

where N_0 is the initial number of nuclei or moles of the isotope, and N_t is the number of nuclei/moles remaining at time *t*. Example 25.5.1 applies these calculations to find the rates of radioactive decay for specific nuclides.

Example 25.5.1: Rates of Radioactive Decay

$^{60}_{27}\text{Co}$ decays with a half-life of 5.27 years to produce $^{60}_{28}\text{Ni}$.

a. What is the decay constant for the radioactive disintegration of cobalt-60?
b. Calculate the fraction of a sample of the $^{60}_{27}\text{Co}$ isotope that will remain after 15 years.
c. How long does it take for a sample of $^{60}_{27}\text{Co}$ to disintegrate to the extent that only 2.0% of the original amount remains?

Solution

(a) The value of the rate constant is given by:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5.27\ \text{y}} = 0.132\ \text{y}^{-1}$$

(b) The fraction of $^{60}_{27}\text{Co}$ that is left after time t is given by $\frac{N_t}{N_0}$. Rearranging the first-order relationship $N_t = N_0 e^{-\lambda t}$ to solve for this ratio yields:

$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-(0.132/\text{y})(15.0/\text{y})} = 0.138$$

The fraction of $^{60}_{27}\text{Co}$ that will remain after 15.0 years is 0.138. Or put another way, 13.8% of the $^{60}_{27}\text{Co}$ originally present will remain after 15 years.

(c) 2.00% of the original amount of $^{60}_{27}\text{Co}$ is equal to 0.0200 × N_0. Substituting this into the equation for time for first-order kinetics, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) = -\frac{1}{0.132\ \text{y}^{-1}}\ln\left(\frac{0.0200 \times N_0}{N_0}\right) = 29.6\ \text{y}$$

Exercise 25.5.1

Radon-222, $^{222}_{86}\text{Rn}$, has a half-life of 3.823 days. How long will it take a sample of radon-222 with a mass of 0.750 g to decay into other elements, leaving only 0.100 g of radon-222?

Answer available at the end of this section.

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of $^{209}_{83}\text{Bi}$ is 1.9 × 10^{19} years; $^{239}_{94}\text{Ra}$ is 24,000 years; $^{222}_{86}\text{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5 × 10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in Table 25.5.1, and others are listed in Appendix N1.

Table 25.5.1: Half-lives of Radioactive Isotopes Important to Medicine

Type	Decay Mode	Half-Life	Uses
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m[1]	γ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

The "m" in Tc-99m stands for "metastable," indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of "dating" the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is radiometric dating and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called radiocarbon dating or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: $^{12}_{6}\mathrm{C}$, which constitutes about 99% of the carbon on earth; $^{13}_{6}\mathrm{C}$, about 1% of the total; and trace amounts of $^{14}_{6}\mathrm{C}$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H}$$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of $^{14}_{6}\mathrm{CO}_2$ to $^{12}_{6}\mathrm{CO}_2$ depends on the ratio of $^{14}_{6}\mathrm{CO}$ to $^{12}_{6}\mathrm{CO}$ in the atmosphere. The natural abundance of $^{14}_{6}\mathrm{CO}$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of $^{14}_{6}\mathrm{C}$ $^{14}_{6}\mathrm{CO}_2$ and $^{12}_{6}\mathrm{CO}_2$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}\mathrm{C}:\ {}^{12}_{6}\mathrm{C}$ ratio found in a living plant is the same as the $^{14}_{6}\mathrm{C}:\ {}^{12}_{6}\mathrm{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}\mathrm{C}$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$$

Thus, the $^{14}_{6}\mathrm{C}:\ {}^{12}_{6}\mathrm{C}$ ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure $25.5.7$ visually depicts this process.

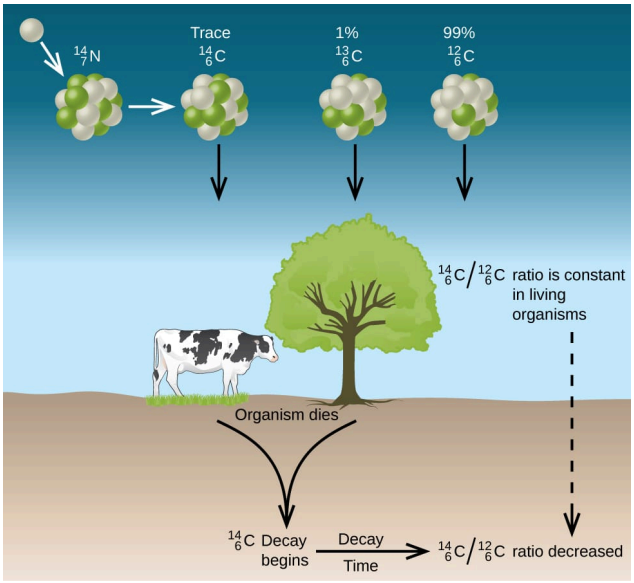


Figure $25.5.7$: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

A diagram shows a cow standing on the ground next to a tree. In the upper left of the diagram, where the sky is represented, a single white sphere is shown and is connected by a downward-facing arrow to a larger sphere composed of green and white spheres that is labeled “superscript 14, subscript 7, N.” This structure is connected to three other structures by a right-facing arrow. Each of the three it points to are composed of green and white spheres and all have arrows pointing from them to the ground. The first of these is labeled “Trace, superscript 14, subscript 6, C,” the second is labeled “1 percent, superscript 13, subscript 6, C” and the last is labeled “99 percent, superscript 12, subscript 6, C.” Two downward-facing arrows that merge into one arrow lead from the cow and tree to the ground and are labeled “organism dies” and “superscript 14, subscript 6, C, decay begins.” A right-facing arrow labeled on top as “Decay” and on bottom as “Time” leads from this to a label of “superscript 14, subscript 6, C, backslash, superscript 12, subscript 6, C, ratio decreased.” Near the top of the tree is a downward facing arrow with the label “superscript 14, subscript 6, C, backslash, superscript 12, subscript 6, C, ratio is constant in living organisms” that leads to the last of the lower statements.

For example, with the half-life of $^{14}_{6}\mathrm{C}$ being 5730 years, if the $^{14}_{6}\mathrm{C}:\ {}^{12}_{6}\mathrm{C}$ ratio in a wooden object found in an archaeological dig is

half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Example 25.5.2: Radiocarbon Dating

A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls has an activity of 10.8 disintegrations per minute per gram of carbon. If the initial C-14 activity was 13.6 disintegrations/min/g of C, estimate the age of the Dead Sea Scrolls.

Solution

The rate of decay (number of disintegrations/minute/gram of carbon) is proportional to the amount of radioactive C-14 left in the paper, so we can substitute the rates for the amounts, *N*, in the relationship:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) \longrightarrow t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right)$$

where the subscript 0 represents the time when the plants were cut to make the paper, and the subscript *t* represents the current time.

The decay constant can be determined from the half-life of C-14, 5730 years:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730\ \text{y}} = 1.21 \times 10^{-4}\ \text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right) = -\frac{1}{1.21 \times 10^{-4}\ \text{y}^{-1}}\ln\left(\frac{10.8\ \text{dis/min/g C}}{13.6\ \text{dis/min/g C}}\right) = 1910\ \text{y}$$

Therefore, the Dead Sea Scrolls are approximately 1900 years old (Figure 25.5.8).



Figure 25.5.8: Carbon-14 dating has shown that these pages from the Dead Sea Scrolls were written or copied on paper made from plants that died between 100 BC and AD 50.

Exercise 25.5.2

More accurate dates of the reigns of ancient Egyptian pharaohs have been determined recently using plants that were preserved in their tombs. Samples of seeds and plant matter from King Tutankhamun's tomb have a C-14 decay rate of 9.07 disintegrations/min/g of C. How long ago did King Tut's reign come to an end?

Answer available at the end of this section.

There have been some significant, well-documented changes to the $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio. The accuracy of a straightforward application of this technique depends on the $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely $^{12}_{6}\text{CO}_2$) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the $^{14}_{6}\text{C}$ has decayed), the ratio of $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ in the atmosphere may be changing. This

manmade increase in $^{12}_{6}CO_2$ in the atmosphere causes the $^{14}_{6}C : \ ^{12}_{6}C$ ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there is additional lead-206 present, which is indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Example 25.5.3: Radioactive Dating of Rocks

An igneous rock contains 9.58×10^{-5} g of U-238 and 2.51×10^{-5} g of Pb-206, and much, much smaller amounts of Pb-208. Determine the approximate time at which the rock formed.

Solution

The sample of rock contains very little Pb-208, the most common isotope of lead, so we can safely assume that all the Pb-206 in the rock was produced by the radioactive decay of U-238. When the rock formed, it contained all of the U-238 currently in it, plus some U-238 that has since undergone radioactive decay.

The amount of U-238 currently in the rock is:

$$9.58 \times 10^{-5} \cancel{\text{g U}} \times \left(\frac{1 \text{ mol U}}{238 \cancel{\text{g U}}} \right) = 4.03 \times 10^{-7} \text{ mol U}$$

Because when one mole of U-238 decays, it produces one mole of Pb-206, the amount of U-238 that has undergone radioactive decay since the rock was formed is:

$$2.51 \times 10^{-5} \cancel{\text{g Pb}} \times \left(\frac{1 \cancel{\text{mol Pb}}}{206 \cancel{\text{g Pb}}} \right) \times \left(\frac{1 \text{ mol U}}{1 \cancel{\text{mol Pb}}} \right) = 1.22 \times 10^{-7} \text{ mol U}$$

The total amount of U-238 originally present in the rock is therefore:

$$4.03 \times 10^{-7} \text{ mol} + 1.22 \times 10^{-7} \text{ mol} = 5.25 \times 10^{-7} \text{ mol U}$$

The amount of time that has passed since the formation of the rock is given by:

$$t = -\frac{1}{\lambda} \ln \left(\frac{N_t}{N_0} \right)$$

with N_0 representing the original amount of U-238 and N_t representing the present amount of U-238.

U-238 decays into Pb-206 with a half-life of 4.5×10^9 y, so the decay constant λ is:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \text{ y}} = 1.54 \times 10^{-10} \text{ y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{1.54 \times 10^{-10} \text{ y}^{-1}} \ln\left(\frac{4.03 \times 10^{-7} \cancel{\text{mol U}}}{5.25 \times 10^{-7} \cancel{\text{mol U}}}\right) = 1.7 \times 10^9 \text{ y}$$

Therefore, the rock is approximately 1.7 billion years old.

Exercise 25.5.3

A sample of rock contains 6.14 × 10^{-4} g of Rb-87 and 3.51 × 10^{-5} g of Sr-87. Calculate the age of the rock. (The half-life of the β decay of Rb-87 is 4.7 × 10^{10} y.)

Answer available at the end of this section.

Summary

Nuclei that have unstable n:p ratios undergo spontaneous radioactive decay. The most common types of radioactivity are α decay, β decay, γ emission, positron emission, and electron capture. Nuclear reactions also often involve γ rays, and some nuclei decay by electron capture. Each of these modes of decay leads to the formation of a new nucleus with a more stable n:p ratio. Some substances undergo radioactive decay series, proceeding through multiple decays before ending in a stable isotope. All nuclear decay processes follow first-order kinetics, and each radioisotope has its own characteristic half-life, the time that is required for half of its atoms to decay. Because of the large differences in stability among nuclides, there is a very wide range of half-lives of radioactive substances. Many of these substances have found useful applications in medical diagnosis and treatment, determining the age of archaeological and geological objects, and more.

Key Equations

- decay rate = λN
- $t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$

Glossary

alpha (α) decay
loss of an alpha particle during radioactive decay

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

daughter nuclide
nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

electron capture
combination of a core electron with a proton to yield a neutron within the nucleus

gamma (γ) emission
decay of an excited-state nuclide accompanied by emission of a gamma ray

half-life ($t_{1/2}$)
time required for half of the atoms in a radioactive sample to decay

parent nuclide
unstable nuclide that changes spontaneously into another (daughter) nuclide

positron emission
(also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

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

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

radiometric dating
use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

Answers

Exercise 25.5.1

11.1 days

Exercise 25.5.2

about 3350 years ago, or approximately 1340 BC

Exercise 25.5.3

3.7×10^9 y

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25.6: Energetics of 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:

$$E = mc^2 \tag{25.6.1}$$

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 25.6.1, 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:

$$\mathrm{C(graphite)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta H^\circ = -393.5 \ \mathrm{kJ/mol} \tag{25.6.2}$$

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

$$\Delta E = (\Delta m)c^2 \tag{25.6.3}$$

we can rearrange the equation to obtain the following relationship between the change in mass and the change in energy:

$$\Delta m = \frac{\Delta E}{c^2} \tag{25.6.4}$$

Because 1 J = 1 (kg•m^2)/s^2, the change in mass is as follows:

$$\Delta m = \frac{-393.5 \ \mathrm{kJ/mol}}{(2.998 \times 10^8 \ \mathrm{m/s})^2} = \frac{-3.935 \times 10^5 (\mathrm{kg \cdot m^2})/(\mathrm{s^2 \cdot mol})}{(2.998 \times 10^8 \ \mathrm{m/s})^2} = -4.38 \times 10^{-12} \ \mathrm{kg/mol} \tag{25.6.5}$$

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:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + {}^{0}_{-1}\beta \tag{25.6.6}$$

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):

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} \tag{25.6.7}$$

$$= 14.003074 \text{ amu} - 14.003242 \text{ amu} = -0.000168 \text{ amu} \tag{25.6.8}$$

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 = -1.68×10^{-4} g = -1.68×10^{-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:

$$\Delta E = (\Delta m)c^2 = (-1.68 \times 10^{-7} \text{ kg})(2.998 \times 10^{8} \text{ m/s})^2 \tag{25.6.9}$$

$$= -1.51 \times 10^{10} (\text{kg} \cdot \text{m}^2)/\text{s}^2 = -1.51 \times 10^{10} \text{ J} = -1.51 \times 10^{7} \text{ kJ} \tag{25.6.10}$$

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 25.6.1

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 25.6.4 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:

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} = (\text{mass } {}^{234}\text{Th} + \text{mass } {}^{4}_{2}\text{He}) - \text{mass } {}^{238}\text{U} \tag{25.6.11}$$

$$= (234.043601 \text{ amu} + 4.002603 \text{ amu}) - 238.050788 \text{ amu} = -0.004584 \text{ amu} \tag{25.6.12}$$

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 25.6.1

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:

$$m_{^2\text{H}} = m_{\text{neutron}} + m_{\text{proton}} + m_{\text{electron}} \tag{25.6.13}$$

$$= 1.008665\ \text{amu} + 1.007276\ \text{amu} + 0.000549\ \text{amu} = 2.016490\ \text{amu} \tag{25.6.14}$$

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 25.6.4, this release of energy must be accompanied by a decrease in the mass of the nucleus.

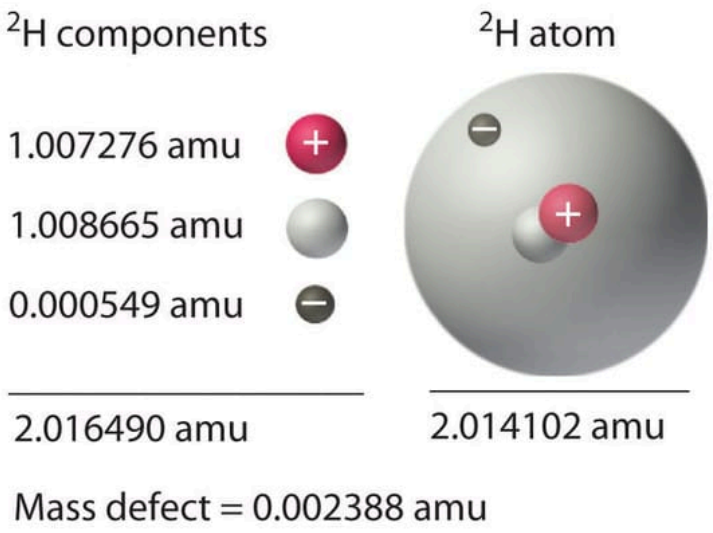


Figure 25.6.1: Nuclear Binding Energy in Deuterium. The mass of a ^{2}H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the mass defect, the greater the nuclear binding 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 25.6.1). 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 25.6.2, 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.

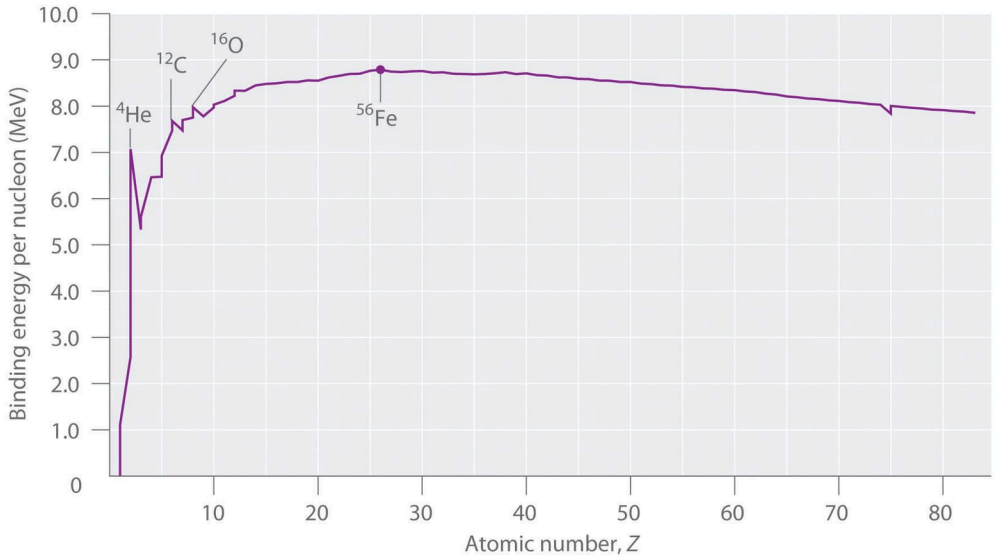


Figure 25.6.2: The Curve of Nuclear Binding Energy. This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light 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 25.6.2) should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 25.6.2) 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 25.6.2

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 25.6.2

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 25.6.1

$\Delta m = -2.0 \times 10^{-5}$ amu; $\Delta E = -1.9 \times 10^{6}$ kJ/mol = −19 keV/atom

Exercise 25.6.2

1800 MeV/^{238}U; 7.57 MeV/nucleon

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25.7: Nuclear Stability

Learning Objectives

- To understand the factors that affect 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 25.7.1). All stable nuclei except the hydrogen-1 nucleus (^{1}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 25.7.1: 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 25.7.2. 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 25.7.2: 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, www.nndc.bnl.gov/chart.

As shown in Figure 25.7.3, 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 25.7.3: The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability.

Note

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 25.7.2, 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.

Example 25.7.1

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 25.7.2, 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 25.7.1

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. radioactive
b. stable
c. radioactive
d. stable

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.

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25.8: 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 25.8.1.

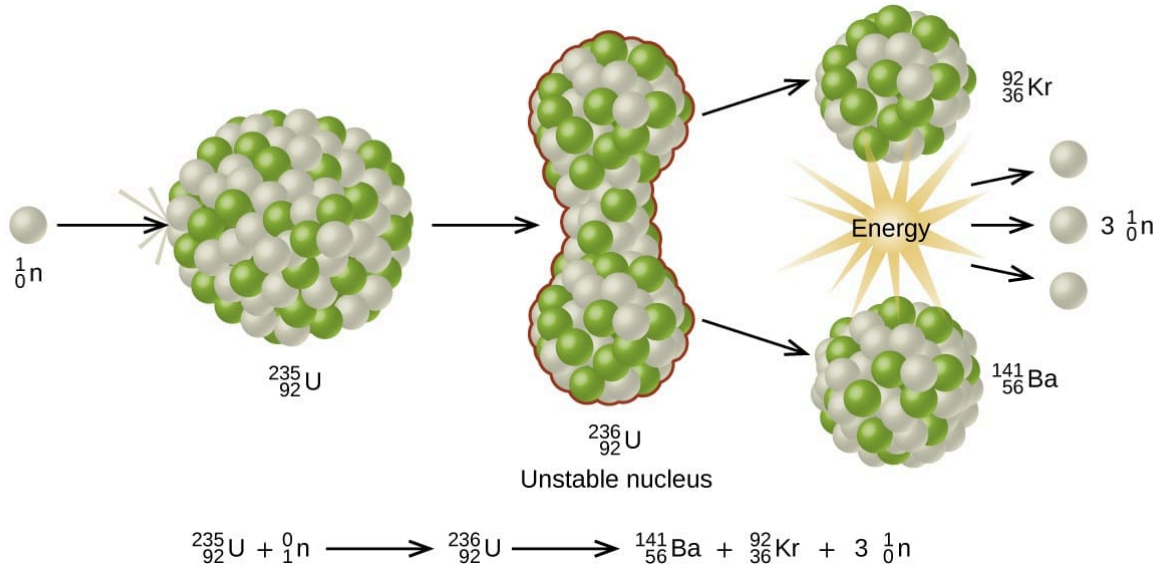


Figure 25.8.1: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount 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 25.8.2. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow {}^{90}_{38}\text{Sr} + {}^{144}_{54}\text{Xe} + 2\ {}^{1}_{0}\text{n}$$

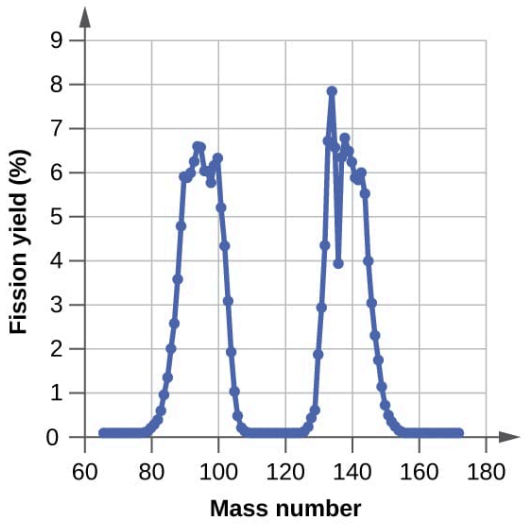
$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow {}^{87}_{35}\text{Br} + {}^{146}_{57}\text{La} + 3\ {}^{1}_{0}\text{n}$$

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow {}^{96}_{37}\text{Rb} + {}^{137}_{55}\text{Cs} + 3\ {}^{1}_{0}\text{n}$$

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow {}^{137}_{52}\text{Te} + {}^{97}_{40}\text{Zr} + 2\ {}^{1}_{0}\text{n}$$

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3\ {}^{1}_{0}\text{n}$$

(a)



(b)

Figure 25.8.2: (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 25.8.3). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

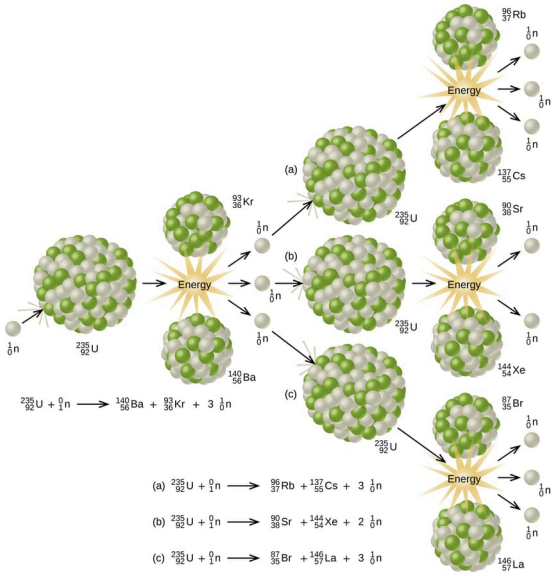


Figure 25.8.3: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

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 25.8.4).

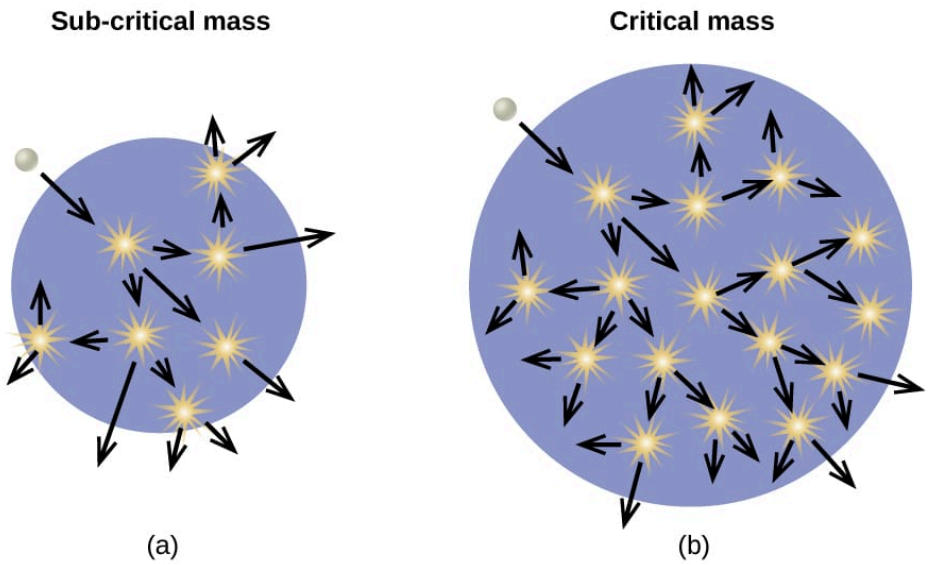


Figure 25.8.4: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (Figure 25.8.5) 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.

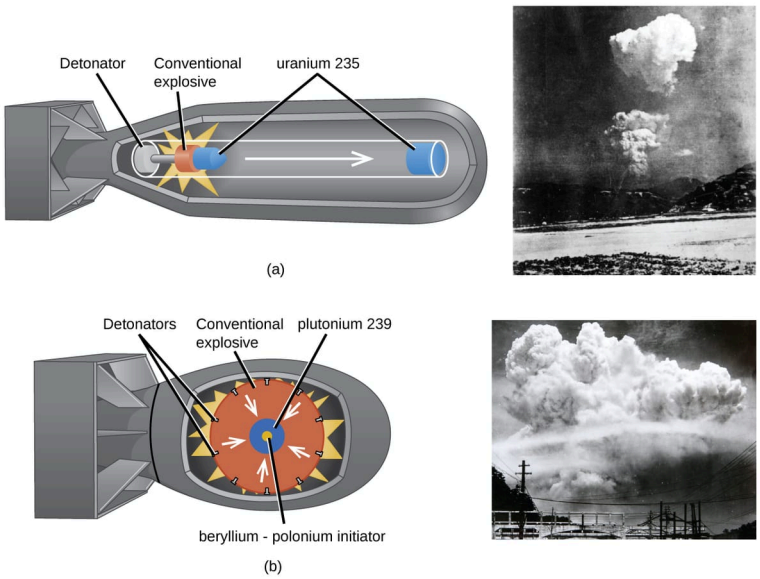


Figure 25.8.5: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb 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 25.8.6). 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.

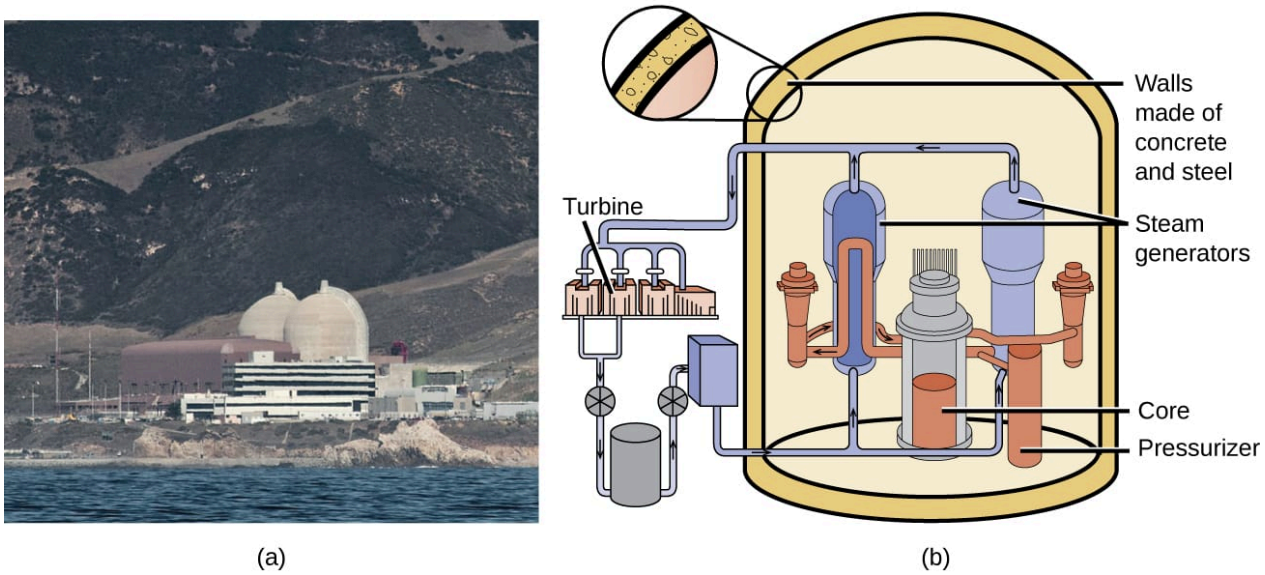


Figure 25.8.6: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water 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 25.8.4). 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 25.8.8) 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:

$$ {}^{10}_{5}\mathrm{B} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He} \tag{25.8.1} $$

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.

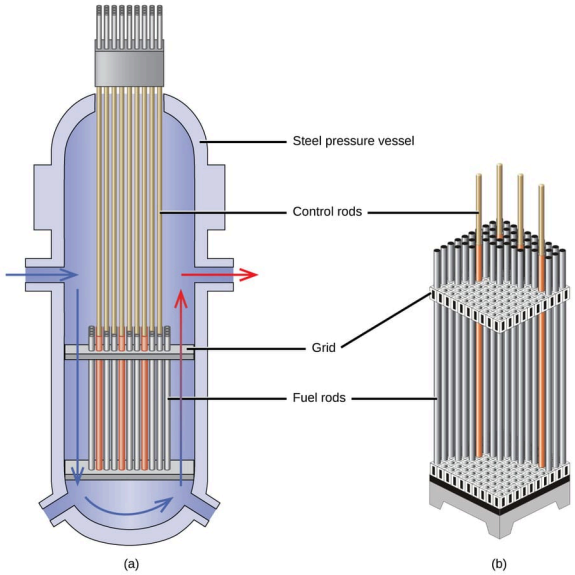


Figure 25.8.7: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, glossary.periodni.com/glossar...en=control+rod)

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 $25.8.1$***:*** *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:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g) \tag{25.8.2}$$

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 $25.8.8$).

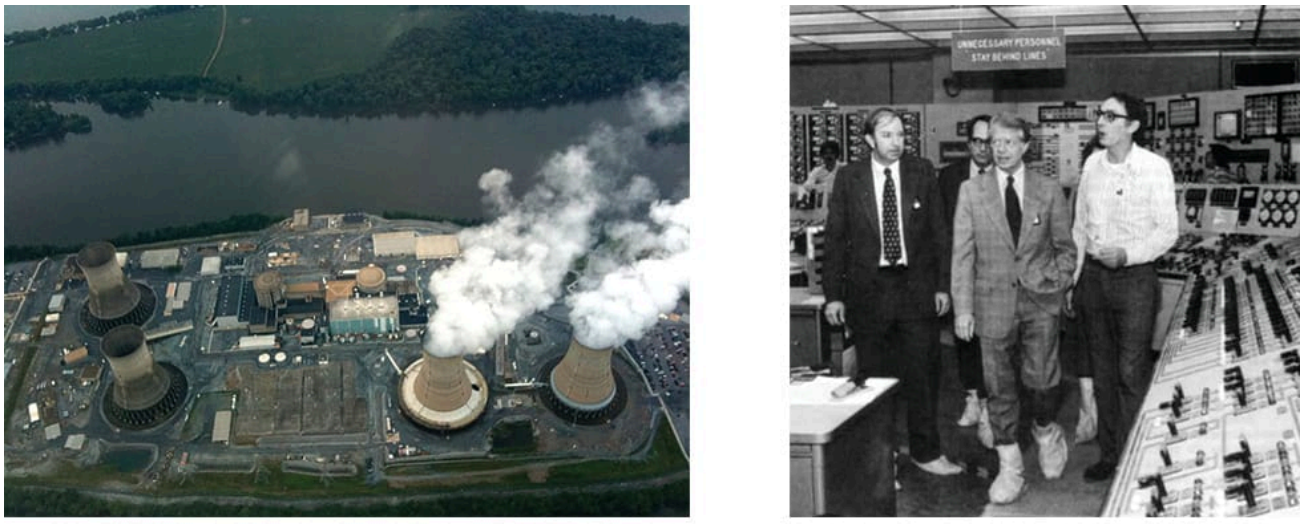


Figure 25.8.8: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control 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 25.8.10).



Figure 25.8.9: (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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25.9: 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:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{n} \tag{25.9.1}$$

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:

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n} \tag{25.9.2}$$

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.

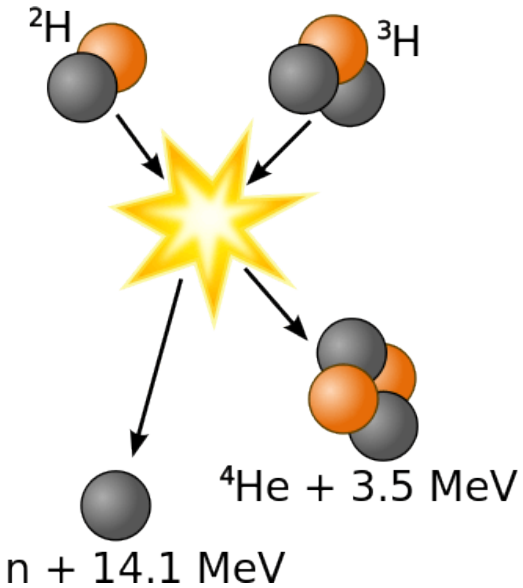


Figure 25.9.1: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of 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 25.9.2).

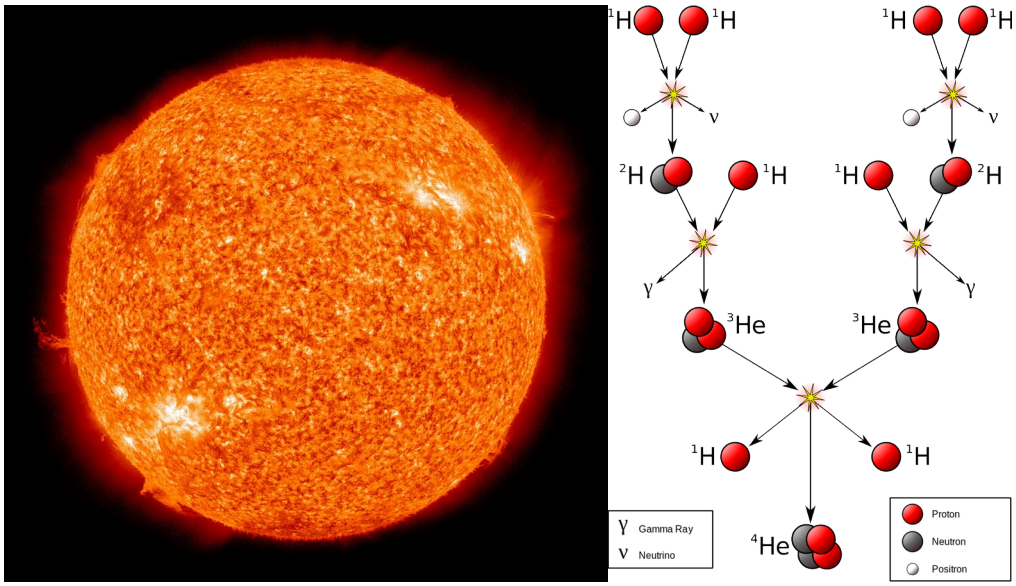


Figure 25.9.2: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

Example 25.9.1

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.

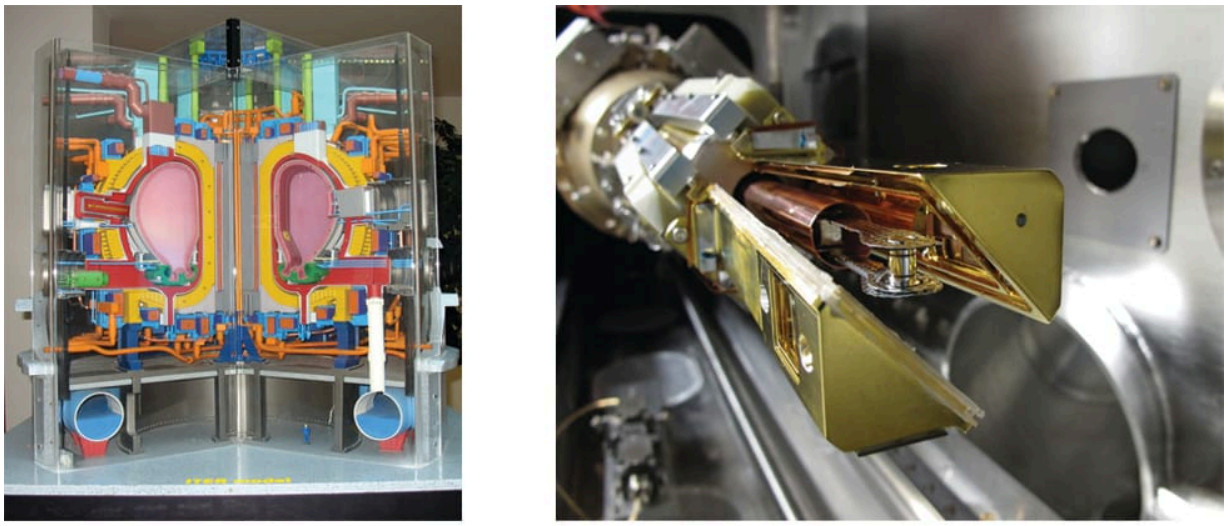


Figure 25.9.3: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving 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 25.9.3). 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

- 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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25.10: Effect of Radiation on Matter

Learning Objectives

- Describe the biological impact of ionizing radiation.
- Define units for measuring radiation exposure.
- Explain the operation of common tools for detecting radioactivity.
- List common sources of radiation exposure in the US.

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 25.10.1).

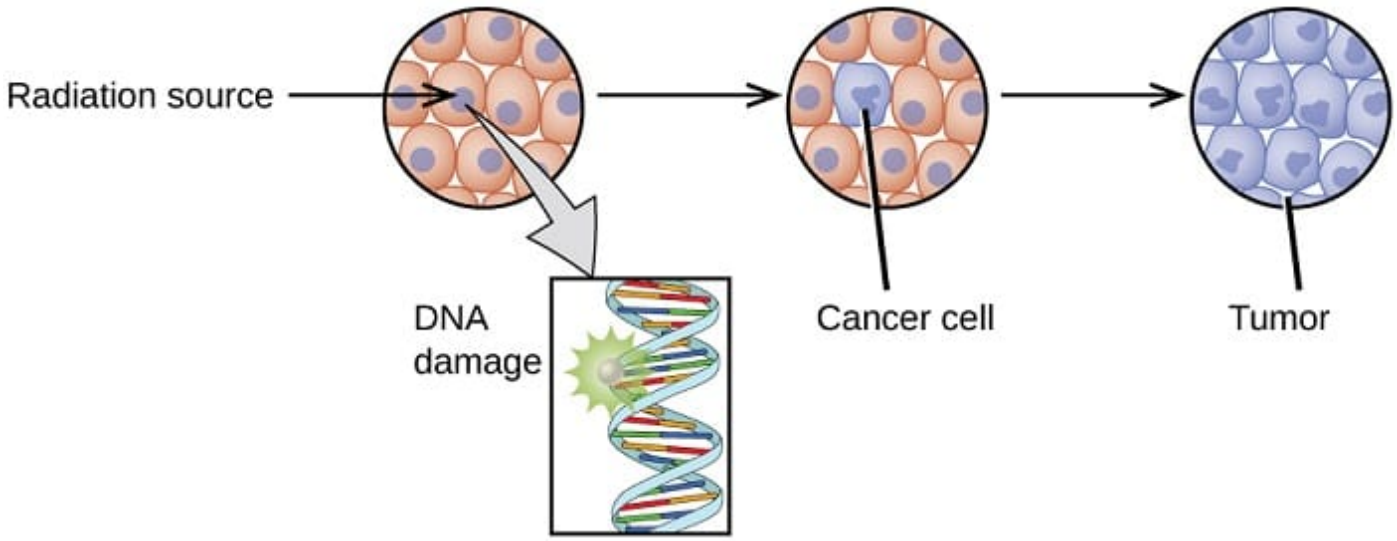


Figure 25.10.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

A diagram is shown which has a white sphere followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres. The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a pair of smaller spheres which are collections of the same white and green spheres. A starburst pattern lies between these two spheres and has three right-facing arrows leading from it to two white spheres and a circle full of ten smaller, peach-colored circles with purple dots in their centers. An arrow leads downward from this circle to a box that contains a helical shape with a starburst near its top left side and is labeled "D N A damage." A right-facing arrow leads from this circle to a second circle, with nine smaller, peach-colored circles with purple dots in their centers and one fully purple small circle labeled "Cancer cell." A right-facing arrow leads to a final circle, this time full of the purple cells, that is labeled "Tumor."

Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 25.10.2).

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Figure 25.10.2: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

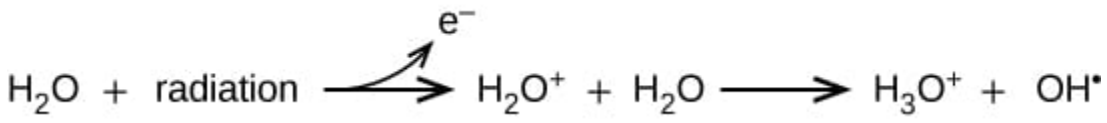


Figure 25.10.3.

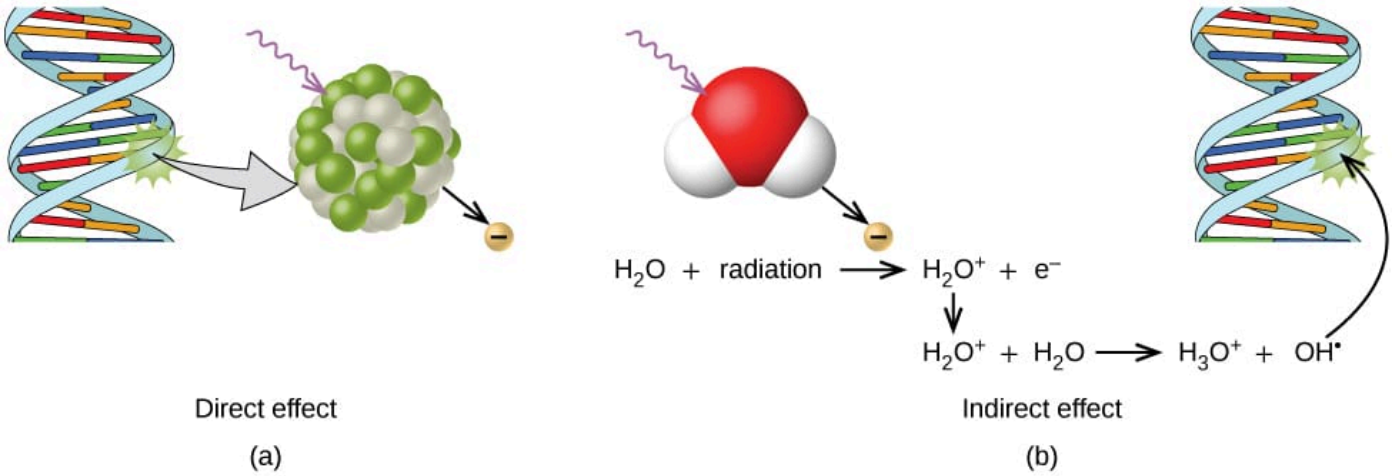


Figure 25.10.3: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure 25.10.4). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

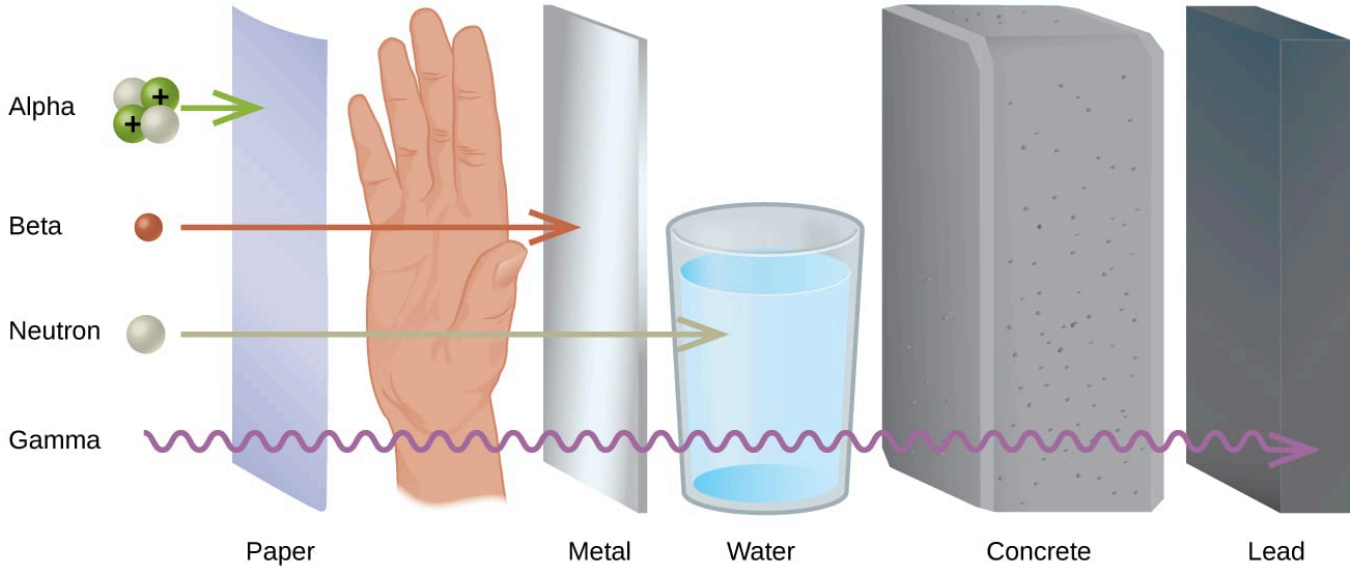


Figure 25.10.4: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

A diagram shows four particles in a vertical column on the left, followed by an upright sheet of paper, a person's hand, an upright sheet of metal, a glass of water, a thick block of concrete and an upright, thick piece of lead. The top particle listed is made up of two white spheres and two green spheres that are labeled with positive signs and is labeled "Alpha." A right-facing arrow leads from this to the paper. The second particle is a red sphere labeled "Beta" and is followed by a right-facing arrow that passes through the paper and stops at the hand. The third particle is a white sphere labeled "Neutron" and is followed by a right-facing arrow that passes through the paper, hand and metal but is stopped at the glass of water. The fourth particle is shown by a squiggly arrow and it passes through all of the substances but stops at the lead. Terms at the bottom read, from left to right, "Paper," "Metal," "Water," "Concrete" and "Lead."

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 25.10.5).

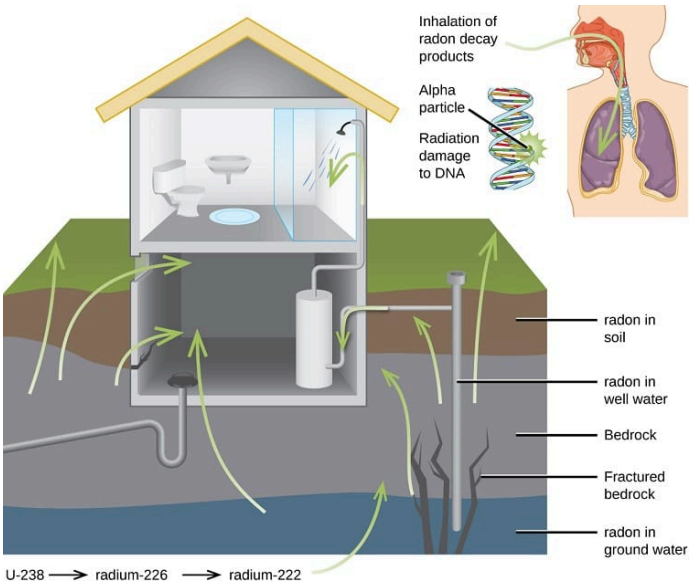


Figure 25.10.5: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

A cut-away image of the side of a house and four layers of the ground it rests on is shown, as well as a second cut-away image of a person's head and chest cavity. The house is shown with a restroom on the second floor and a basement with a water heater as the first floor. Green arrows lead from the lowest ground layer, labeled "radon in ground water," from the third ground layer, labeled "Bedrock" and "Fractured bedrock," from the second layer, labeled "radon in well water," and from the top layer, labeled "radon in soil to the inside of the basement area. In the smaller image of the torso, a green arrow is shown to enter the person's nasal passage and travel to the lungs. This is labeled "Inhalation of radon decay products." A small coiled, helical structure next to the torso is labeled "alpha particle" on one section where it has a starburst pattern and "Radiation damage to D N A" on another segment.

Radon is found in buildings across the country, with amounts dependent on location. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the level found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 25.10.6). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

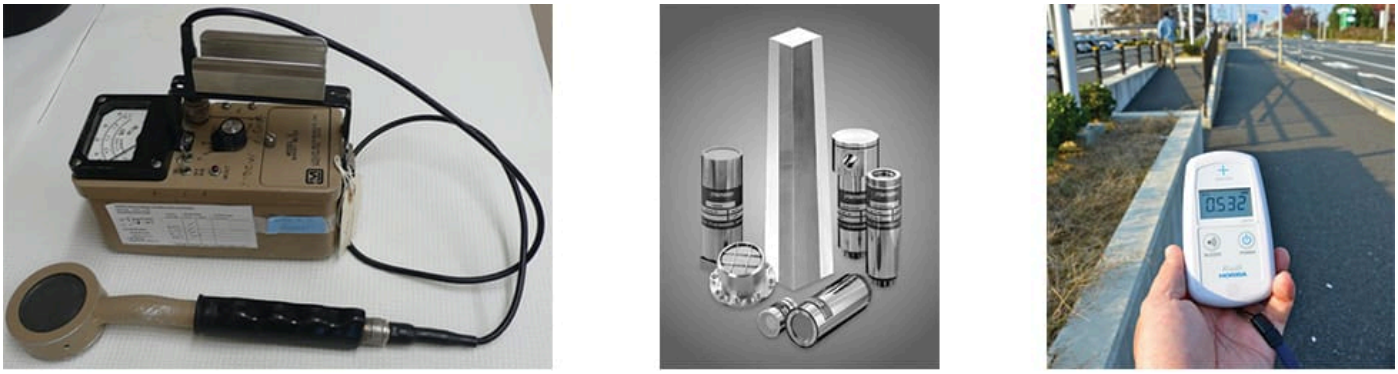


Figure 25.10.6: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (Credit c: modification of work by "osaMu"/Wikimedia commons.)

Three photographs are shown and labeled "a," "b" and "c." Photo a shows a Geiger counter sitting on a table. It is made up of a metal box with a read-out screen and a wire leading away from the box connected to a sensor wand. Photograph b shows a collection of tall and short vertical tubes arranged in a grouping while photograph c shows a person's hand holding a small machine with a digital readout while standing on the edge of a roadway.

A variety of units are used to measure various aspects of radiation (Table 25.10.1). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7×10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

Table 25.10.1: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7×10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for man (rem)		Rem = RBE × rad

The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy), along with a biological factor referred to as the RBE (for relative biological effectiveness), that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{25.10.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

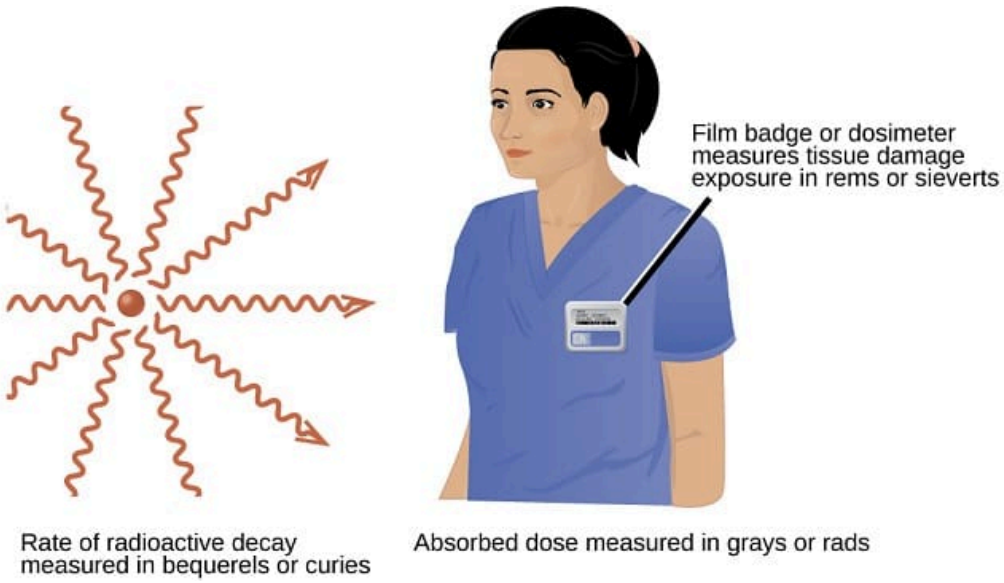


Figure 25.10.7: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC by 4.0; OpenStax)

Two images are shown. The first, labeled “Rate of radioactive decay measured in becquerels or curies,” shows a red sphere with ten red squiggly arrows facing away from it in a 360 degree circle. The second image shows the head and torso of a woman wearing medical scrubs with a badge on her chest. The caption to the badge reads “Film badge or dosimeter measures tissue damage exposure in rems or sieverts” while a phrase under this image states “Absorbed dose measured in grays or rads.”

Example 25.10.1: Amount of Radiation

Cobalt-60 ($t_{1/2}$ = 5.26 y) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

a. What is its activity in Bq?
b. What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity} = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N = \left(\frac{\ln 2}{5.26\ \text{y}}\right) \times 5.00\ \text{g} = 0.659\ \frac{\text{g}}{\text{y}}\ \text{of}\ {}^{60}\text{Co that decay}$$

And to convert this to decays per second:

$$0.659\ \frac{\text{g}}{\text{y}} \times \frac{\text{y}}{365\ \text{day}} \times \frac{1\ \text{day}}{24\ \text{hours}} \times \frac{1\ \text{h}}{3,600\ \text{s}} \times \frac{1\ \text{mol}}{59.9\ \text{g}} \times \frac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} \times \frac{1\ \text{decay}}{1\ \text{atom}}$$

$$= 2.10 \times 10^{14}\ \frac{\text{decay}}{\text{s}}$$

(a) Since $1\ \text{Bq} = 1\ \frac{\text{decay}}{\text{s}}$, the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Bq}}{1\ \frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\ \text{Bq}$$

(b) Since $1\ \text{Ci} = 3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}$, the activity in curie (Ci) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Ci}}{3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}}\right) = 5.7 \times 10^{2}\ \text{Ci}$$

Exercise 25.10.1

Tritium is a radioactive isotope of hydrogen ($t_{1/2} = 12.32$ years) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

Answer a available at the end of this section.

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure 25.10.8, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

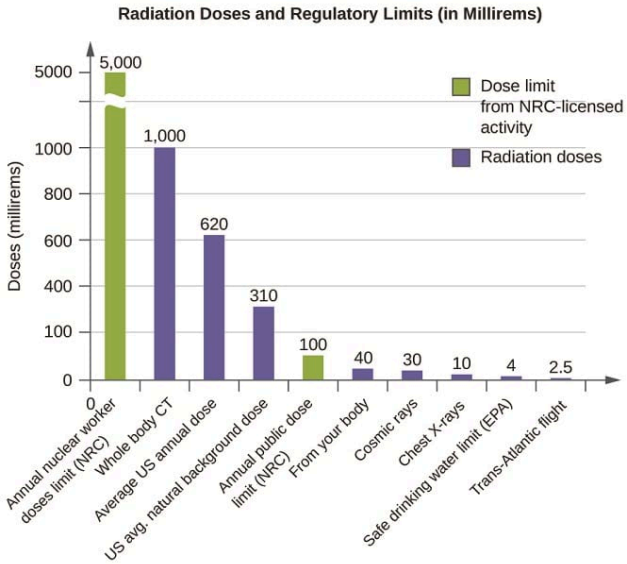


Figure 25.10.8: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A bar graph titled “Radiation Doses and Regulatory Limits, open parenthesis, in Millirems, close parenthesis” is shown. The y-axis is labeled “Doses in Millirems” and has values from 0 to 5000 with a break between 1000 and 5000 to indicate a different scale to the top of the graph. The y-axis is labeled corresponding to each bar. The first bar, measured to 5000 on the y-axis, is drawn in red and is labeled “Annual Nuclear Worker Doses Limit, open parenthesis, N R C, close parenthesis.” The second bar, measured to 1000 on the y-axis, is drawn in blue and is labeled “Whole Body C T” while the third bar, measured to 620 on the y-axis, is drawn in blue and is labeled “Average U period S period Annual Dose.” The fourth bar, measured to 310 on the y-axis, is drawn in blue and is labeled “U period S period Natural Background Dose” while the fifth bar, measured to 100 on the y-axis and drawn in red reads “Annual Public Dose Limit, open parenthesis, N R C, close parenthesis.” The sixth bar, measured to 40 on the y-axis, is drawn in blue and is labeled “From Your Body” while the seventh bar, measured to 30 on the y-axis and drawn in blue reads “Cosmic rays.” The eighth bar, measured to 4 on the y-axis, is drawn in blue and is labeled “Safe Drinking Water Limit, open parenthesis, E P A, close parenthesis” while the ninth bar, measured to 2.5 on the y-axis and drawn in red reads “Trans Atlantic Flight.” A legend on the graph shows that red means “Dose Limit From N R C dash licensed activity” while blue means “Radiation Doses.”

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person’s lifetime, which is another reason why

it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table 25.10.2.

Table 25.10.2: Health Effects of Radiation

Exposure (rem)	Health Effect	Time to Onset (Without Treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Summary

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating, but potentially most damaging, and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source of radiation, and limiting time of exposure.

Footnotes

1. 1 Source: US Environmental Protection Agency

Glossary

becquerel (Bq)
SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s.

curie (Ci)
Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

Geiger counter
Instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube.

gray (Gy)
SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue.

ionizing radiation
Radiation that can cause a molecule to lose an electron and form an ion.

millicurie (mCi)
Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

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.

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.

relative biological effectiveness (RBE)
Measure of the relative damage done by radiation.

roentgen equivalent man (rem)
Unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv.

scintillation counter
Instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation.

sievert (Sv)
SI unit measuring tissue damage caused by radiation; takes energy and biological effects of radiation into account.

Answers

Exercise 25.10.1

$3.56 \times 10^{11}\text{Bq}$

$0.962\ \text{Ci}$

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25.11: Applications of Radioisotopes

Learning Objectives

- List common applications of radioactive isotopes

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism. Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}\mathrm{Tc}$), thallium-201 ($^{201}_{81}\mathrm{Tl}$), iodine-131 ($^{131}_{53}\mathrm{I}$), and sodium-24 ($^{24}_{11}\mathrm{Na}$). Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure $25.11.1$) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.

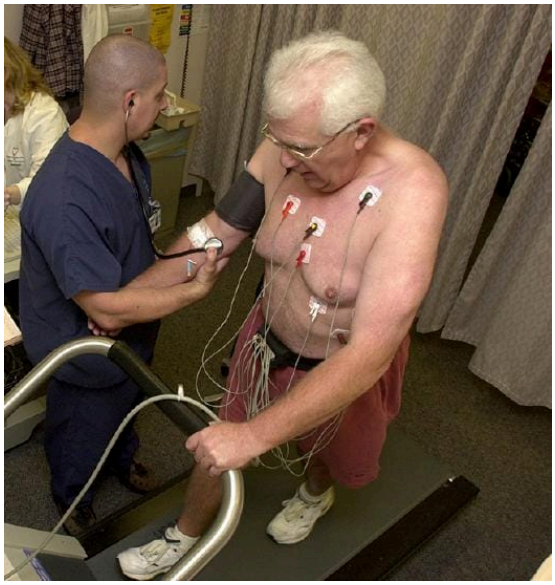


Figure $25.11.1$: Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "BlueOctane"/Wikimedia Commons)

A medical professional is assisting a topless elderly man on a treadmill with sensors and electrical wires connected to his torso.

Radioisotopes used in medicine typically have short half-lives—for example, the ubiquitous Tc-99m has a half-life of 6.01 hours. This makes Tc-99m essentially impossible to store and prohibitively expensive to transport, so it is made on-site instead. Hospitals and other medical facilities use Mo-99 (which is primarily extracted from U-235 fission products) to generate Tc-99. Mo-99 undergoes β decay with a half-life of 66 hours, and the Tc-99 is then chemically extracted (Figure $25.11.2$). The parent nuclide Mo-99 is part of a molybdate ion, $\mathrm{MoO_4}^{2-}$; when it decays, it forms the pertechnetate ion, $\mathrm{TcO_4}^{-}$. These two water-soluble ions are separated by column chromatography, with the higher charge molybdate ion adsorbing onto the alumina in the column, and the lower charge pertechnetate ion passing through the column in the solution. A few micrograms of Mo-99 can produce enough Tc-99 to perform as many as 10,000 tests.

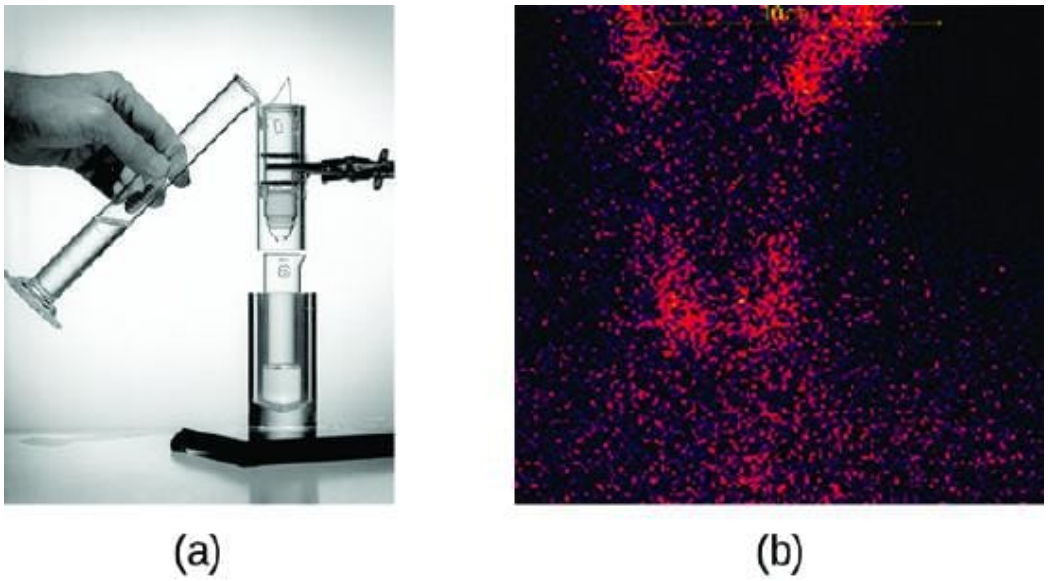


Figure 25.11.2: (a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The MoO_4^{2-} *is retained by the matrix in the column, whereas the* TcO_4^- *passes through and is collected. (b) Tc-99 was used in this scan of the neck of a patient with Grave's disease. The scan shows the location of high concentrations of Tc-99. (credit a: modification of work by the Department of Energy; credit b: modification of work by "MBq"/Wikimedia Commons)*

The first image shows a hand pouring a liquid from a measuring cylinder into a column held up by a clamp. Below the column is a glass tube. The second picture shows red dots on a dark background dispersed everywhere with four spots of heavily concentrated regions.

Radioisotopes can also be used, typically in higher doses than as a tracer, as treatment. Radiation therapy is the use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing (Figure 25.11.3). A cancer patient may receive external beam radiation therapy delivered by a machine outside the body, or internal radiation therapy (brachytherapy) from a radioactive substance that has been introduced into the body. Note that chemotherapy is similar to internal radiation therapy in that the cancer treatment is injected into the body, but differs in that chemotherapy uses chemical rather than radioactive substances to kill the cancer cells.

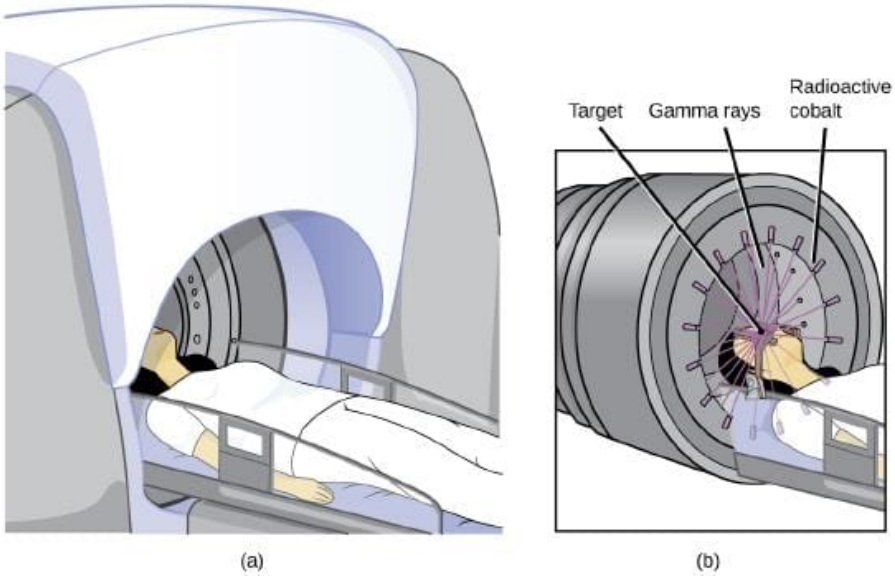


Figure 25.11.3: The cartoon in (a) shows a cobalt-60 machine used in the treatment of cancer. The diagram in (b) shows how the gantry of the Co-60 machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

A. A woman lies down as she goes into a dome shaped medical machine. B. A closer view of the women's head shows gamma rays from radioactive cobalt attacks the target on the woman's head.

Cobalt-60 is a synthetic radioisotope produced by the neutron activation of Co-59, which then undergoes β decay to form Ni-60,

along with the emission of γ radiation. The overall process is:

$$^{59}_{27}\mathrm{Co} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{60}_{27}\mathrm{Co} \longrightarrow {}^{60}_{28}\mathrm{Ni} + {}^{0}_{-1}\beta + 2{}^{0}_{0}\gamma$$

The overall decay scheme for this is shown graphically in Figure 25.11.4.

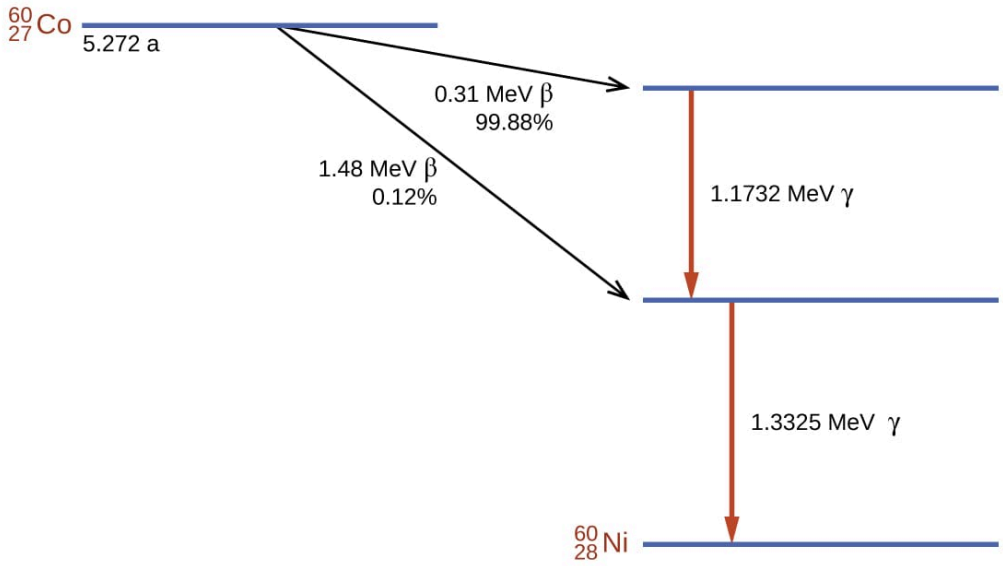


Figure 25.11.4: Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

Radioisotopes are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope C-14 was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(l) \longrightarrow \mathrm{C_6H_{12}O_6}(s) + 6\,\mathrm{O_2}(g),$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of ${}^{14}_{6}\mathrm{C}$. At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Commercial applications of radioactive materials are equally diverse (Figure 25.11.5). They include determining the thickness of films and thin metal sheets by exploiting the penetration power of various types of radiation. Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring. Many foods are preserved by radiation that kills microorganisms that cause the foods to spoil.



Figure 25.11.5: Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

A. A man is observing a monitor which shows the X-ray of luggages. B. Many apples on processing belts.

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure 25.11.6). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

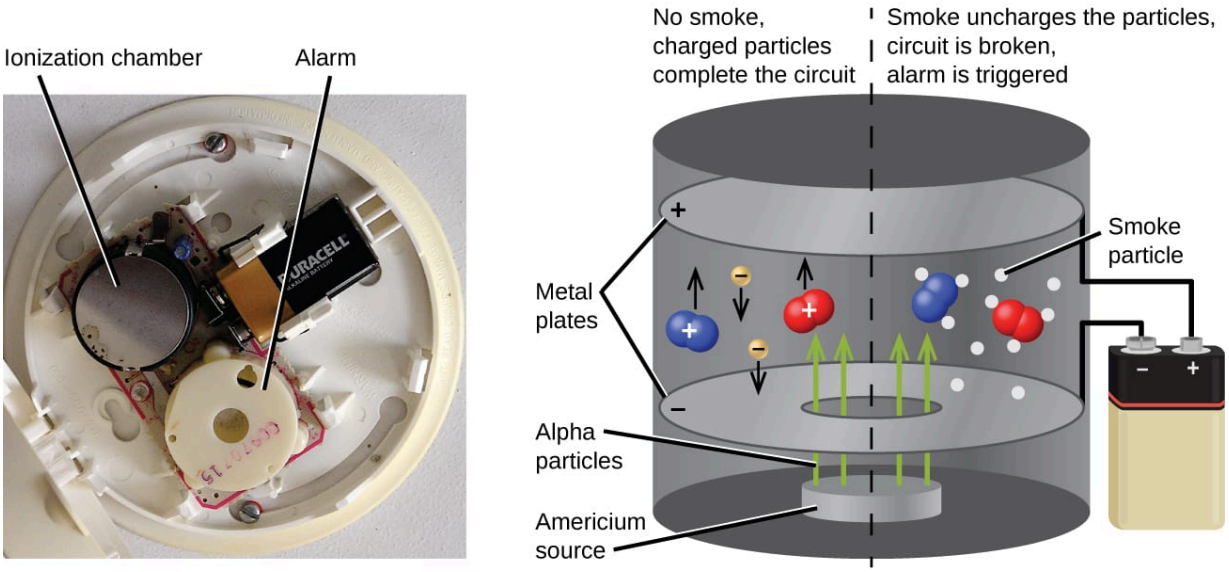


Figure 25.11.6: Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

The inside of a smoke detector is shown with the alarm and ionization chamber labeled. In the picture beside it, a schematic shows the mechanisms of a smoke detector. The two oppositely charged metals plates in the detector are shown along with the Americium source on the bottom part emitting alpha particles. The schematic is divided into two parts, one to show the presence and the other for the absence of smoke.

Summary

Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more. Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications. Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US. Most of these radioisotopes have relatively short half-lives; some are short enough that the radioisotope must be made on-site at medical facilities. Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be

delivered externally or internally.

Glossary

chemotherapy
similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

external beam radiation therapy
radiation delivered by a machine outside the body

internal radiation therapy
(also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

radiation therapy
use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive tracer
(also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

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25.E: Exercises

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26: STRUCTURE OF ORGANIC COMPOUNDS

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

- Topic hierarchy

26.1: Organic Compounds and Structures: An Overview
26.2: Alkanes
26.3: Cycloalkanes
26.4: Stereoisomerism in Organic Compounds
26.5: Alkenes and Alkynes
26.6: Aromatic Hydrocarbons
26.7: Organic Compounds Containing Functional Groups
26.8: From Molecular Formula to Molecular Structure

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26.1: Organic Compounds and Structures: An Overview

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.
- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.
- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.
- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names
- To describe functional groups and explain why they are useful in the study of organic chemistry.

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.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{26.1.1}$$

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.

Note

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 26.1.1.

Table 26.1.1: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane	Inorganic	NaCl
low melting points	−95°C	high melting points	801°C

Organic	Hexane	Inorganic	NaCl
low boiling points	69°C	high boiling points	1,413°C
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 26.1.1 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 26.1.1.

Hydrocarbons

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). *Saturated*, 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.

Note

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 26.1.1.

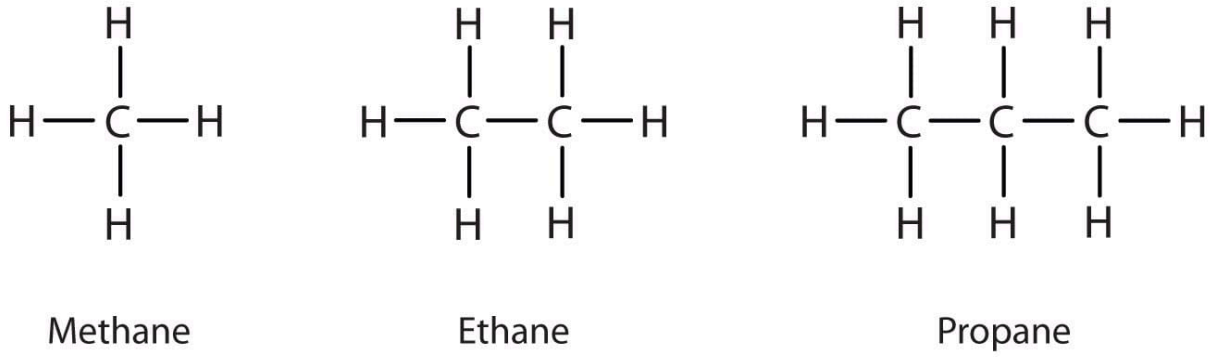


Figure 26.1.1: The Three Simplest Alkanes

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 26.1.2).

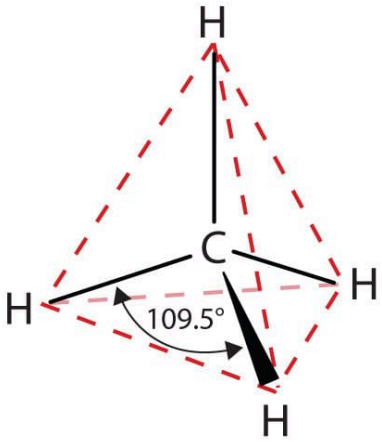


Figure 26.1.2: The Tetrahedral Methane Molecule

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 26.1.2.

Table 26.1.2: 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 26.1.3. 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.

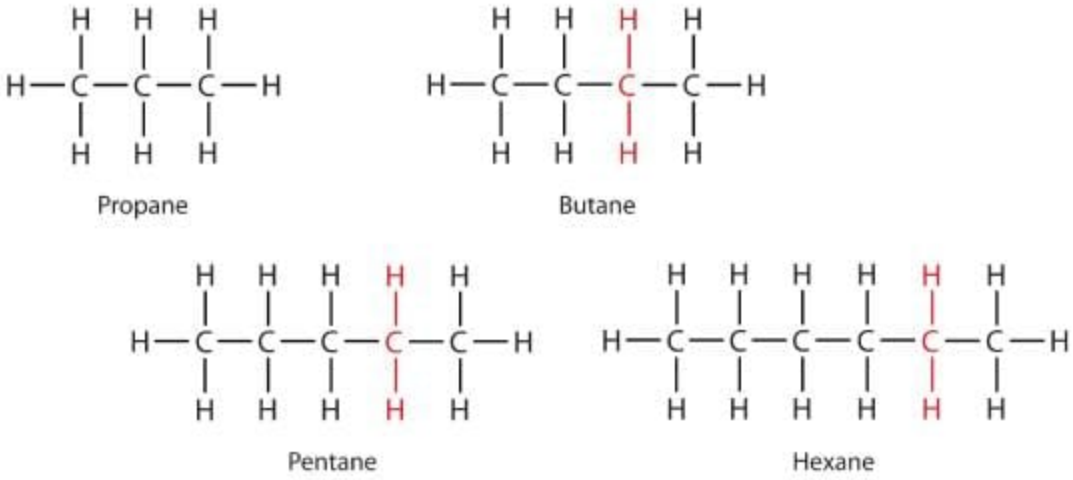
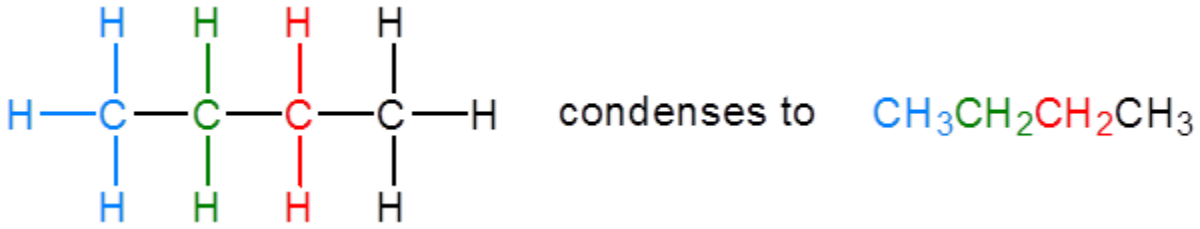


Figure 26.1.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

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 $C_8H_{(2 \times 8) + 2} = C_8H_{18}$.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and isobutane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms. Unfortunately, structural formulas are difficult to type/write and take up a lot of space. Chemists often use condensed structural formulas to alleviate these problems. The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:



The ultimate condensed formula is a line-angle formula, in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:



Note

Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Nomenclature

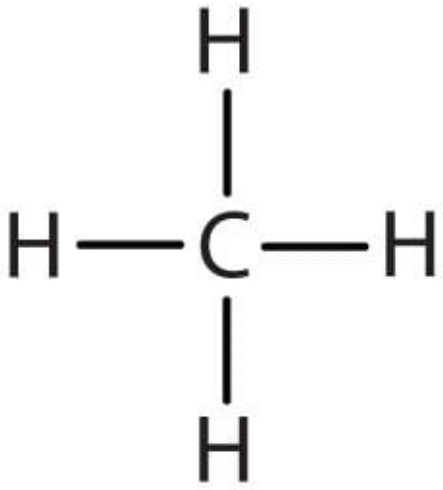
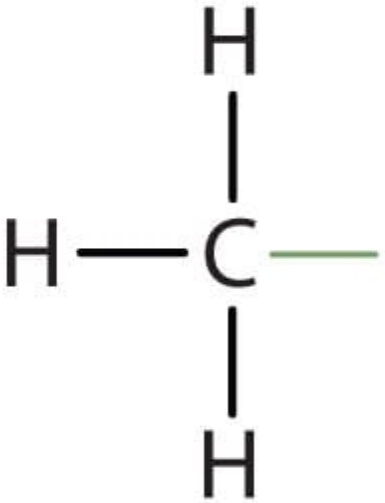
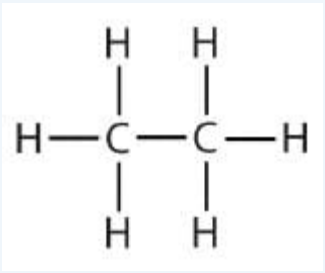
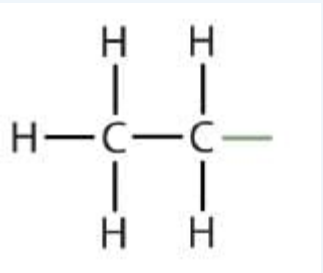
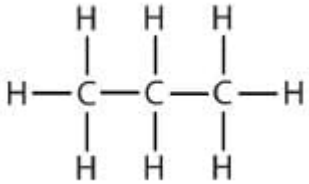
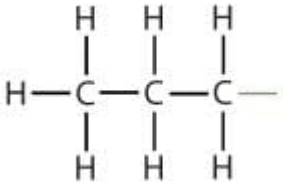
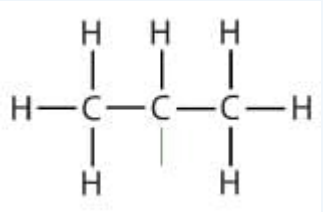
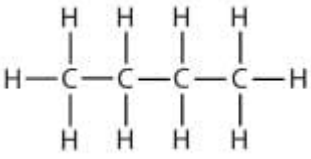
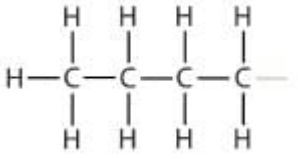
As noted in Table 26.1.2:, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.) A stem name (Table 26.1.3) indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers. For now, we will consider only those substituents called alkyl groups.

Table 26.1.3: Stems That Indicate the Number of Carbon Atoms in Organic Molecules

Stem	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the CH_3 group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table 26.1.4. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

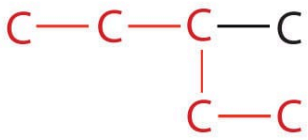
Table 26.1.4: Common Alkyl Groups

Parent Alkane		Alkyl Group		C
methane		methyl		
ethane		ethyl		
propane		propyl		CI
		isopropyl		(
butane		butyl*		CH_3

***There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where ap**

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 26.1.1).

1. **Name alkanes according to the LCC of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.
2. **If the hydrocarbon is branched, number the carbon atoms of the LCC.** Numbers are assigned in the direction that gives the lowest numbers to the carbon atoms with attached substituents. Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other. (The LCC need not be written in a straight line; for example, the LCC in the following has five carbon atoms.)

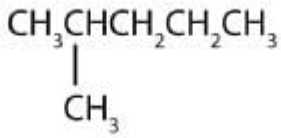
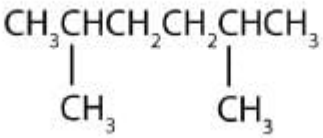
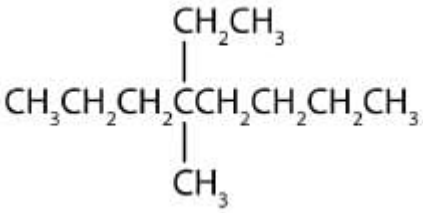


3. **Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

Example 26.1.1

Name each compound.

1. 
2. 
3. 

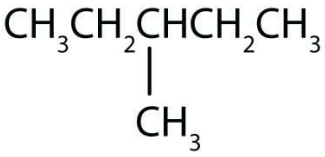
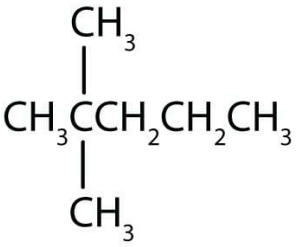
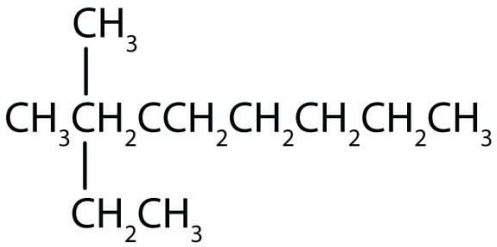
Solution

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.

2. The LCC has six carbon atoms, so the parent compound is hexane (rule 1). Methyl groups (rule 2) are attached to the second and fifth carbon atoms. The name is 2,5-dimethylhexane.
3. The LCC has eight carbon atoms, so the parent compound is octane (rule 1). There are methyl and ethyl groups (rule 2), both attached to the fourth carbon atom (counting from the *right* gives this carbon atom a lower number; rule 3). The correct name is thus 4-ethyl-4-methyloctane.

Exercise 26.1.1

Name each compound.

1. 
2. 
3. 

Example 26.1.2

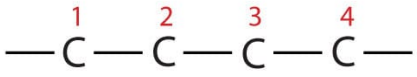
Draw the structure for each compound.

1. 2,3-dimethylbutane
2. 4-ethyl-2-methylheptane

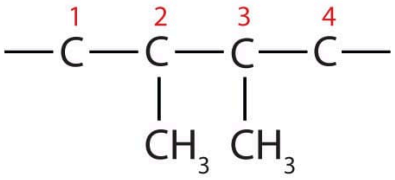
Solution

In drawing structures, always start with the parent chain.

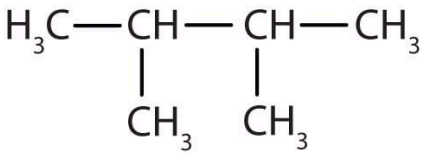
1. The parent chain is butane, indicating four carbon atoms in the LCC.



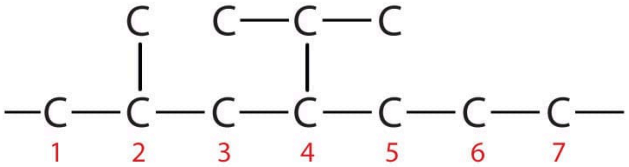
Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (CH_3) groups, one on the second carbon atom and one on the third.



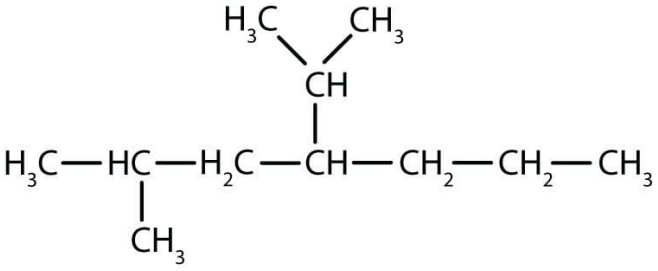
Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.



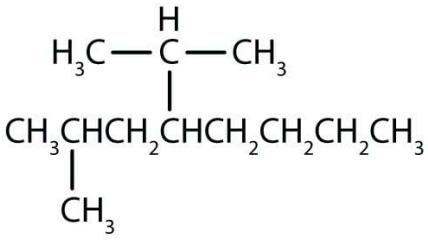
2. Adding the groups at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas:



or



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

Exercise 26.1.2

Draw the structure for each compound.

1. 4-ethyloctane
2. 3-ethyl-2-methylpentane
3. 3,3,5-trimethylheptane

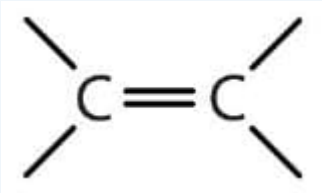
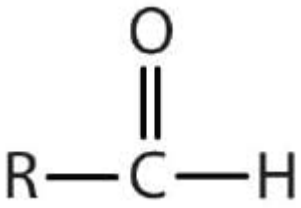
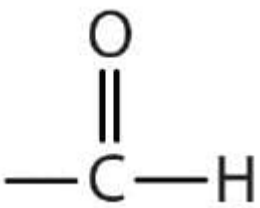
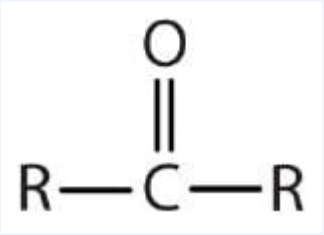
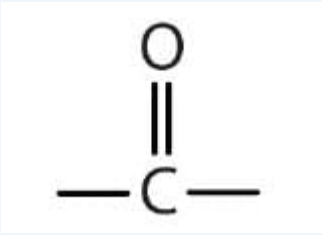
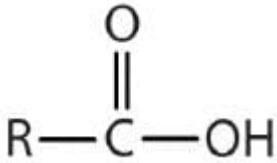
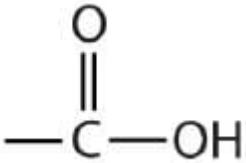
Functional Groups

Functional groups are atoms or small groups of atoms (two to four) that exhibit a characteristic reactivity. A particular functional group will almost always display its characteristic chemical behavior when it is present in a compound. Because of their importance in understanding organic chemistry, functional groups have characteristic names that often carry over in the naming of individual compounds incorporating specific groups. In our study of organic chemistry, it will become extremely important to be able to quickly recognize the most common functional groups, because they are the key structural elements that define

how organic molecules react. For now, we will only worry about drawing and recognizing each functional group, as depicted by Lewis and line structures. Much of the remainder of your study of organic chemistry will be taken up with learning about how the different functional groups tend to behave in organic reactions.

Previously, we considered several kinds of hydrocarbons. Now we examine some of the many organic compounds that contain functional groups. We first introduced the idea of the functional group, a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule. If you understand the behavior of a particular functional group, you will know a great deal about the general properties of that class of compounds. In this chapter, we make a brief yet systematic study of some of organic compound families. Each family is based on a common, simple functional group that contains an oxygen atom or a nitrogen atom. Some common functional groups are listed in Table 26.1.5 and a more comprehensive list if found here.

Table 26.1.5: Selected Organic Functional Groups

Name of Family	General Formula	Functional Group	Suffix*
alkane	RH	none	*-ane*
alkene	$R_2C{=}CR_2$		*-ene*
alkyne	RC≡CR	–C≡C–	*-yne*
alcohol	ROH	–OH	*-ol*
thiol	RSH	–SH	*-thiol*
ether	ROR	–O–	ether
aldehyde			*-al*
ketone			*-one*
carboxylic acid			*-oic acid*

***Ethers do not have a suffix in their common name; all ethers end with the word *ether*.**

Summary

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.
- Alkanes have both common names and systematic names, specified by IUPAC.
- The functional group, a structural arrangement of atoms and/or bonds, is largely responsible for the properties of organic compound families.

Contributors and Attributions

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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26.2: Alkanes

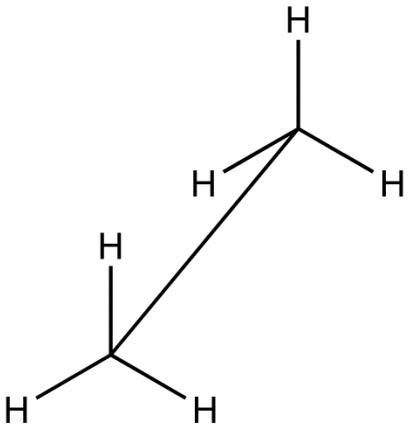
Alkanes are organic compounds that consist entirely of single-bonded carbon and hydrogen atoms and lack any other functional groups. Alkanes have the general formula C_nH_{2n+2} and can be subdivided into the following three groups: the **linear straight-chain alkanes**, **branched alkanes**, and **cycloalkanes**. Alkanes are also *saturated hydrocarbons*.

Conformation

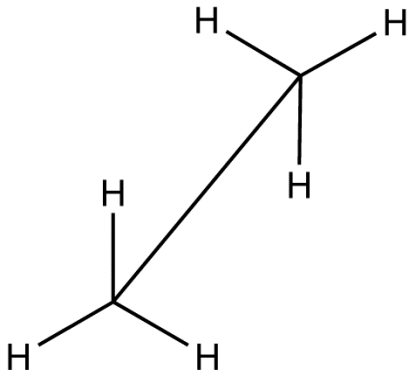
When we smell something, the information travels to us via molecules, and almost always these are organic molecules. These molecules can be detected by a variety of organs, including noses in dogs and antennae in crickets, but no matter what organ is sensing the smell, one of the crucial factors in determining how an organism reacts to a compound is the shape of the molecule. The sense of smell depends on thousands of different receptors in the organ, working conceptually on a lock-and-key basis: a molecule with a given shape can fit into a given receptor, and when it does, a signal is sent telling the nervous system that the organism has encountered that particular type of molecule, and the organism reacts appropriately.

What gives a molecule its shape? Given a structural formula, could you determine the shape of the corresponding molecule in three dimensions? Could you predict its biological activity, including not only its smell, but also a host of other behaviors linked to the shape of molecular messengers, such as anti-cancer activity or narcotic properties? These questions are at the cutting edge of biological chemistry. Although they are best answered through computer modeling, we can develop some of the qualitative ideas used in these models.

A conformation of an acyclic molecule is a specific disposition of atoms in the molecule in space within the molecule due to free rotation around bonds (e.g., ethane (CH_3CH_3)). Due to free rotation around the carbon-carbon bond, the ethane molecule could assume an infinite number of conformations, two of which are shown below as saw-horse formulas.

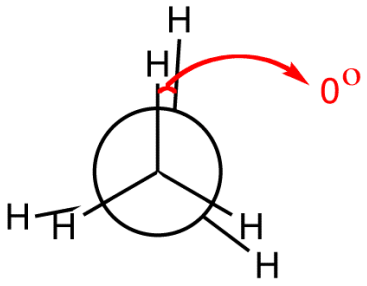


eclipsed conformation

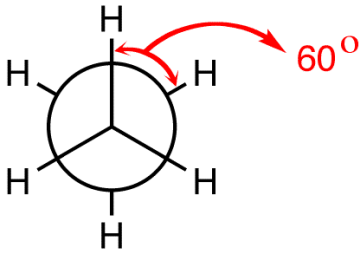


staggered conformation

In the eclipsed conformation of ethane the smallest dihedral angle is 0°, whereas in the staggered conformation it is 60°, which can be seen more clearly in the respective Newman projection.



eclipsed conformation



staggered conformation

Figure 26.2.1).

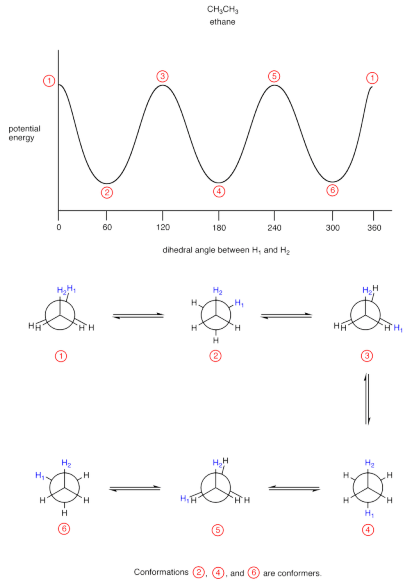


Figure 26.2.1: Shown below is the potential energy diagram of conformations of ethane.

Conformations of Butane

In the case of ethane, conformational changes are very subtle, but in others they are more obvious. Butane ($CH_3CH_2CH_2CH_3$) has four tetrahedral carbons and three carbon-carbon bonds connecting them together. Let's number the carbons along the chain C1, C2, C3 and C4. Rotating around the C-C bonds connected to the terminal carbons -- C1-C2 and C3-C4 -- only subtle changes in shape would be apparent. However, rotating about C2-C3 produces some pretty obvious shape changes.

Pay attention to where the two methyl groups are with respect to each other. If we call C1-C2-C3-C4 the dihedral angle, then at 0 degrees the molecule is in an eclipsed conformation, apparent when looking at the Newman projection. Looked at from other vantage points, the molecule is curled up into the shape of a letter C (Figure 26.2.2).

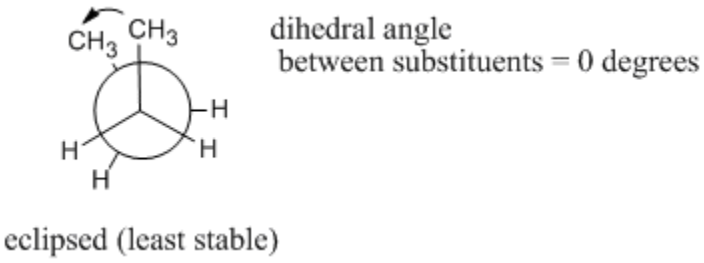


Figure 26.2.2: A three-dimensional model of butane. This C-shape that it adopts here is called the "least-stable eclipsed" conformation.

At 60 degrees, the molecule is no longer eclipsed, and just as in ethane the energy is a little bit lower, but the overall shape when

viewed from the side is still a sort of twisted C (Figure 26.2.3).

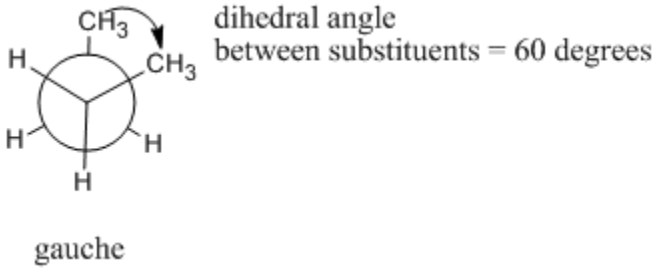


Figure 26.2.3: A three-dimensional model of butane. This shape is called the "gauche conformation".

At 120 degrees the molecule is eclipsed again, but from the side it has now twisted almost into a shape like the letter Z (Figure 26.2.4).

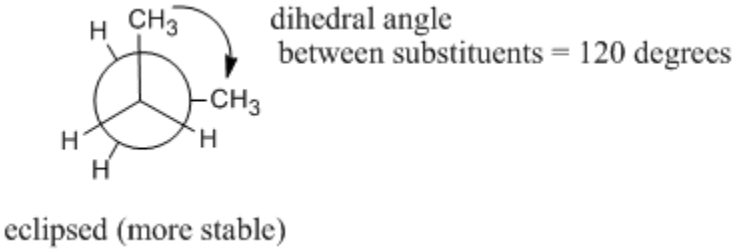


Figure 26.2.4: A three-dimensional model of butane in the "most-stable eclipsed" conformation.

At 180 degrees, the molecule is staggered again and has settled into a regular, zig-zag, letter Z shape.

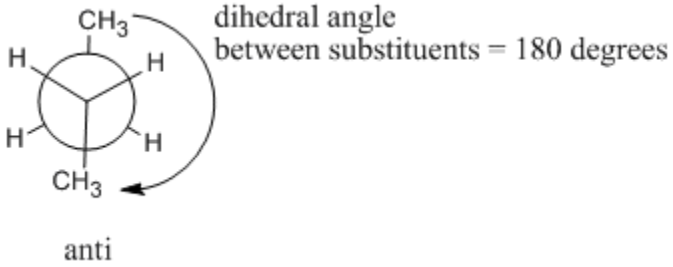


Figure 26.2.5: A three-dimensional model of the "anti conformation" of butane.

These conformations of butane are really pretty different. Which shape would the molecule prefer? From what we learned about ethane, we could probably rule out the eclipsed conformations. Each of those would have 3 kcal/mol of torsional strain.

However, there is another factor that destabilizes the initial conformation at 0 degrees, in favor of the Z-shaped one with the methyl groups 180 degrees apart from each other. This factor is called "sterics" and it refers to the idea that molecules, or parts of molecules, take up space, and so two parts of the butane can't occupy the same place at the same time. Put more simply, sterics refers to crowdedness. When the two methyl groups in butane are too close together, they are too crowded, and they are at higher energy. When they get farther apart, crowding subsides and the energy in the molecule goes down.

- Torsional strain forces bonds on neighboring carbons to be staggered.
- Steric strain forces groups away from each other to relieve crowding.
- Torsion and sterics both contribute to strain energy.
- Strain can be released by getting the molecule in a lower energy conformation.

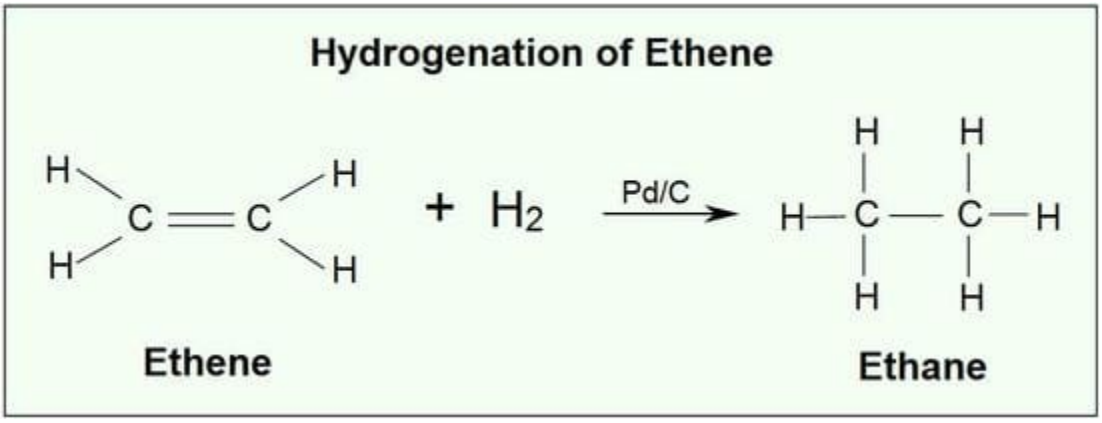
For butane, that means getting those two methyl groups away from each other and keeping the bonds staggered. There is some additional jargon that is used to describe these butane conformations:

- In an anti conformer, the largest groups are 180 degrees from each other.
- In a gauche conformer, the bonds are staggered but the largest groups are 600 from each other.

Preparation of Alkanes

An important way to generate alkanes is the hydrogenation of an alkene (discussed later) The double bond of an alkene consists of a sigma (σ) bond and a pi (π) bond. Because the carbon-carbon π bond is relatively weak, it is quite reactive and can be easily broken and reagents can be added to carbon. Reagents are added through the formation of single bonds to carbon in an addition reaction.

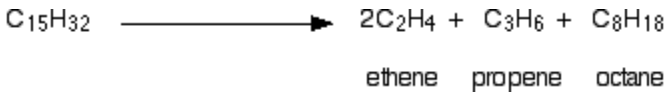
An example of an alkene addition reaction is a process called hydrogenation.In a hydrogenation reaction, two hydrogen atoms are added across the double bond of an alkene, resulting in a saturated alkane. Hydrogenation of a double bond is a thermodynamically favorable reaction because it forms a more stable (lower energy) product. In other words, the energy of the product is lower than the energy of the reactant; thus it is exothermic (heat is released). The heat released is called the heat of hydrogenation, which is an indicator of a molecule's stability.



Although the hydrogenation of an alkene is a thermodynamically favorable reaction, it will not proceed without the addition of a catalyst. Common catalysts used are insoluble metals such as palladium and platinum. Hydrogenation reactions are extensively used to create commercial goods.Hydrogenation is used in the food industry to make a large variety of manufactured goods, like spreads and shortenings, from liquid oils. This process also increases the chemical stability of products and yields semi-solid products like margarine. Hydrogenation is also used in coal processing. Solid coal is converted to a liquid through the addition of hydrogen. Liquefying coal makes it available to be used as fuel.

Alkanes from Petroleum

Cracking is the name given to breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst. The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum). There is not any single unique reaction happening in the cracker. The hydrocarbon molecules are broken up in a fairly random way to produce mixtures of smaller hydrocarbons, some of which have carbon-carbon double bonds. One possible reaction involving the hydrocarbon $C_{15}H_{32}$ might be:



Contributors and Attributions

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26.3: Cycloalkanes

Cyclic systems are a little different from open-chain systems. In an open chain, any bond can be rotated 360 degrees, going through many different conformations. That complete rotation isn't possible in a cyclic system, because the parts that you would be trying to twist away from each other would still be connected together. Cyclic systems have fewer "degrees of freedom" than aliphatic systems; they have "restricted rotation". Because of the restricted rotation of cyclic systems, most of them have much more well-defined shapes than their aliphatic counterparts. Let's take a look at the basic shapes of some common rings. Many biologically important compounds are built around structures containing rings, so it's important that we become familiar with them. In nature, three- to six-membered rings are frequently encountered, so we'll focus on those.

Cyclopropane

A three membered ring has no rotational freedom whatsoever. A plane is defined by three points, so the three carbon atoms in cyclopropane are all constrained to lie in the same plane.



cyclopropane

Furthermore, if you look at a model you will find that the neighboring C-H bonds (C-C bonds, too) are all held in eclipsed conformations. Cyclopropane is always at maximum torsional strain. This strain can be illustrated in a line drawing of cyclopropane as shown from the side. In this oblique view, the dark lines mean that those sides of the ring are closer to you.



However, the ring isn't big enough to introduce any steric strain, which does not become a factor until we reach six membered rings. Until that point, rings are not flexible enough for two atoms to reach around and bump into each other. The really big problem with cyclopropane is that the C-C-C bond angles are all too small.

- All the carbon atoms in cyclopropane appear to be tetrahedral.
- These bond angles ought to be 109 degrees.
- The angles in an equilateral triangle are actually 60 degrees, about half as large as the optimum angle.
- This factor introduces a huge amount of strain in the molecule, called ring strain.

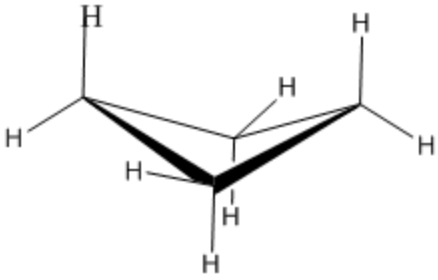
Cyclobutane

Cyclobutane is a four membered ring. In two dimensions, it is a square, with 90 degree angles at each corner.



cyclobutane

However, in three dimensions, cyclobutane is flexible enough to buckle into a "butterfly" shape, relieving torsional strain a little bit. When it does that, the bond angles get a little worse, going from 90 degrees to 88 degrees. In a line drawing, this butterfly shape is usually shown from the side, with the near edges drawn using darker lines.



- With bond angles of 88 rather than 109 degrees, cyclobutane has a lot of ring strain, but less than in cyclopropane.
- Torsional strain is still present, but the neighboring bonds are not exactly eclipsed in the butterfly.
- Cyclobutane is still not large enough that the molecule can reach around to cause crowding. Steric strain is very low.
- Cyclobutanes are a little more stable than cyclopropanes and are also a little more common in nature.

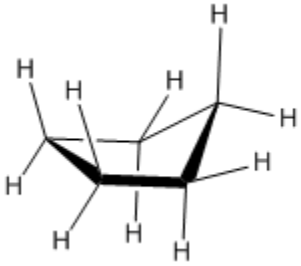
Cyclopentanes

Cyclopentanes are even more stable than cyclobutanes, and they are the second-most common paraffinic ring in nature, after cyclohexanes. In two dimensions, a cyclopentane appears to be a regular pentagon.



cyclopentane

In three dimensions, there is enough freedom of rotation to allow a slight twist out of this planar shape. In a line drawing, this three-dimensional shape is drawn from an oblique view, just like cyclobutane.



The ideal angle in a regular pentagon is about 107 degrees, very close to a tetrahedral bond angle. Cyclopentane distorts only very slightly into an "envelope" shape in which one corner of the pentagon is lifted up above the plane of the other four, and as a result, ring strain is entirely removed. The envelope removes torsional strain along the sides and flap of the envelope. However, the neighbouring carbons are eclipsed along the "bottom" of the envelope, away from the flap. There is still some torsional strain in cyclopentane. Again, there is no steric strain in this system.

Cyclohexane

Cyclohexane is one of the most important cycloalkanes and so is the focus discussion of the conformations of cycloalkanes. If the carbons of a cyclohexane ring were placed at the corners of a regular planar hexagon, all the C-C-C bond angles would have to be 120°. Because the expected normal C-C-C bond angle should be near the tetrahedral value of 109.5°, the suggested planar configuration of cyclohexane would have angle strain at each of the carbons, and would correspond to less stable cyclohexane molecules than those with more normal bond angles. The actual normal value for the C-C-C bond angle of an open-chain $-CH_2-CH_2-CH_2$ unit appears to be about 112.5°, which is 3° greater than the tetrahedral value. From this we can conclude that the angle strain at each carbon of a planar cyclohexane would be (120° — 112.5°) = 1.5°. Angle strain is not the whole story with regard to the instability of the planar form, because in addition to having C-C-C bond angles different from their normal values, the planar structure also has its carbons and hydrogens in the unfavorable eclipsed arrangement, as shown in Figure 12-2. How

both of these factors can be taken into account is illustrated in Exercises 12-2 and 12-3.

Figure 26.3.1: *Cyclohexane in the strained planar configuration showing how the hydrogens become eclipsed*

If the carbon valence angles are kept near the tetrahedral value, you will find that you can construct ball-and-stick models of the cyclohexane six-carbon ring with two quite different conformations. These are known as the “chair” and “boat” conformations (Figure 26.3.1). It has not been possible to separate cyclohexane at room temperature into pure isomeric forms that correspond to these conformations, and actually the two forms appear to be rapidly interconverted. The chair conformation is considerably more stable and comprises more than 99.9% of the equilibrium mixture at room temperature.1

Figure 26.3.1: *Cyclohexane in the strained planar configuration showing how the hydrogens become eclipsed*

Why is the boat form less stable than the chair form, if both have normal C—C—C bond angles? The answer is that the boat form has unfavorable nonbonded interactions between the hydrogen atoms around the ring. If we make all of the bond angles normal and orient the carbons to give the “extreme boat” conformation of Figure 12-4, a pair of 1,4 hydrogens (the so-called “flagpole” hydrogens) have to be very close together (1.83 A).

Table 26.3.1: Strain in Cycloalkane Rings and Heats of Combustion of Cycloalkanes

Compound	n	**Angle Strain at each CH_2**	**Heat of Combustion ΔH^o (kcal/mol)**	**Heat of Combustion ΔH^o per CH_2/N (kcal/mol)**	**Total Strain (kcal/mol)**
ethene	2	109.5	337.2	168.6	22.4
cyclopropane	3	49.5	499.9	166.6	27.7
cyclobutane	4	19.5	655.9	164.0	26.3
cyclopentane	5	1.5	793.4	158.7	6.5
cyclohexane	6	10.5	944.8	157.5	0.4
cycloheptane	7	19.1	1108.1	158.4	6.3
cyclooctane	8	25.5	1268.9	158.6	9.7
cyclononane	9	30.5	1429.5	158.8	12.9
cyclodecane	10	34.5	1586.1	158.6	12.1
cyclopentadecane	15	46.5	2362.5	157.5	1.5
open chain alkane				157.4	-

Contributors and Attributions

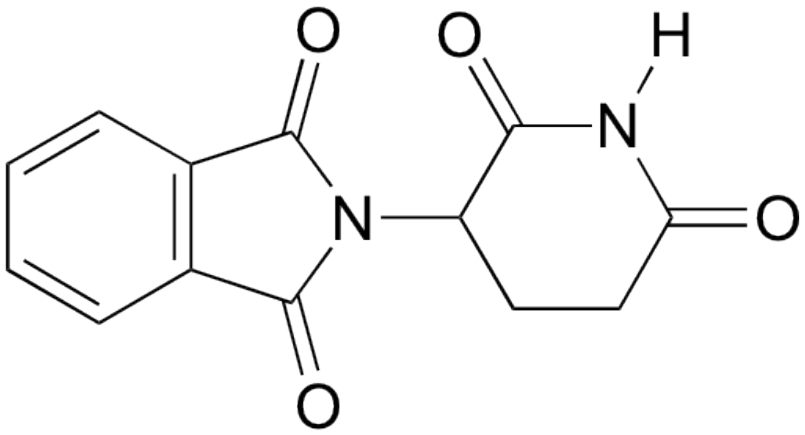
Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition*. W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

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26.4: Stereoisomerism in Organic Compounds

In the 1960's, a drug called thalidomide was widely prescribed in the Western Europe to alleviate morning sickness in pregnant women.



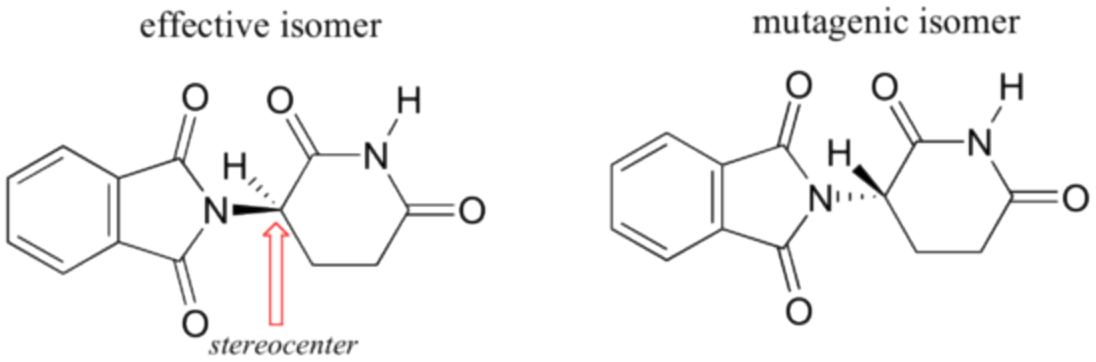
thalidomide

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.

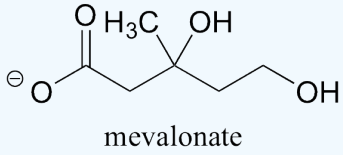


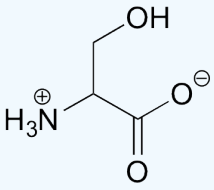
One of the isomers is an effective medication, the other caused the side effects. Both isomeric forms have the same molecular formula and the same atom-to-atom connectivity, so they are not constitutional isomers. Where they differ is in the arrangement in three-dimensional space about one tetrahedral, sp^3-hybridized carbon. These two forms of thalidomide are **stereoisomers**.

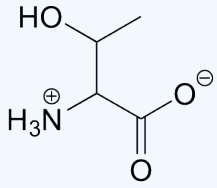
Note that the carbon in question has *four different substituents* (two of these just happen to be connected by a ring structure). Tetrahedral carbons with four different substituent groups are called **stereocenters**.

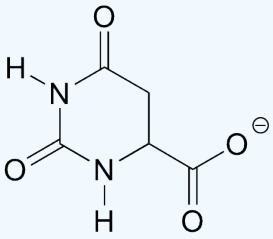
Example 26.4.1

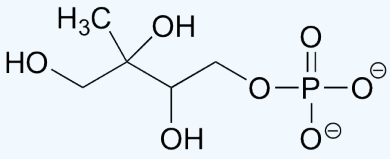
Locate all of the carbon stereocenters in the molecules below.

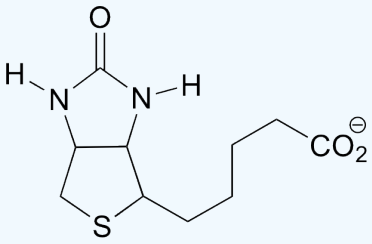

mevalonate


serine


threonine

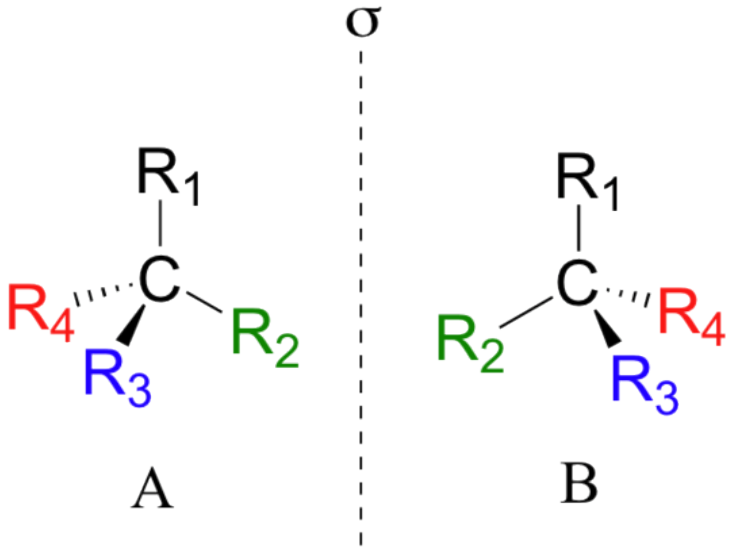

dihydroorotate


2-methylerythritol-4-phosphate

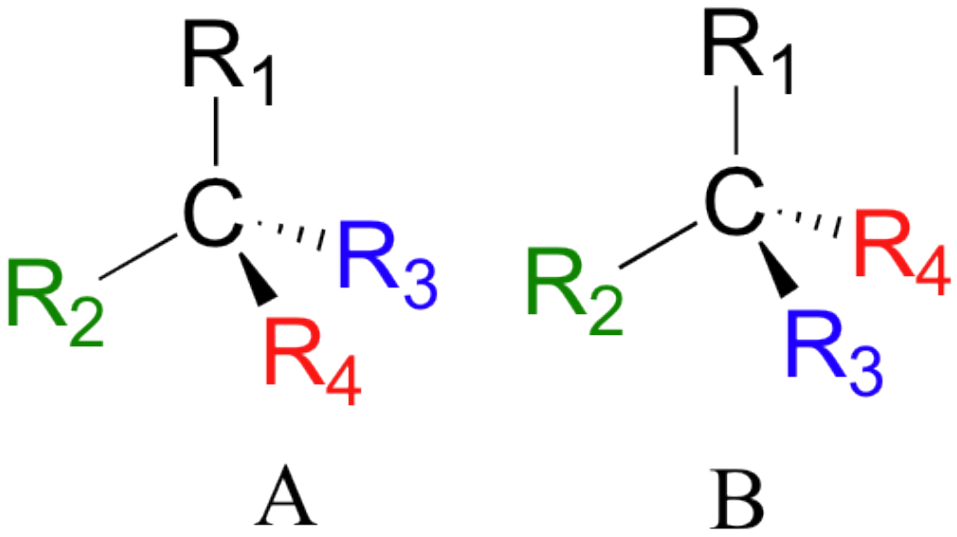

biotin

Solution

Looking at the structures of what we are referring to as the two isomers of thalidomide, you may not be entirely convinced that they are actually two different molecules. In order to convince ourselves that they are indeed different, let's create a generalized picture of a tetrahedral carbon stereocenter, with the four substituents designated R_1-R_4. The two stereoisomers of our simplified model look like this:

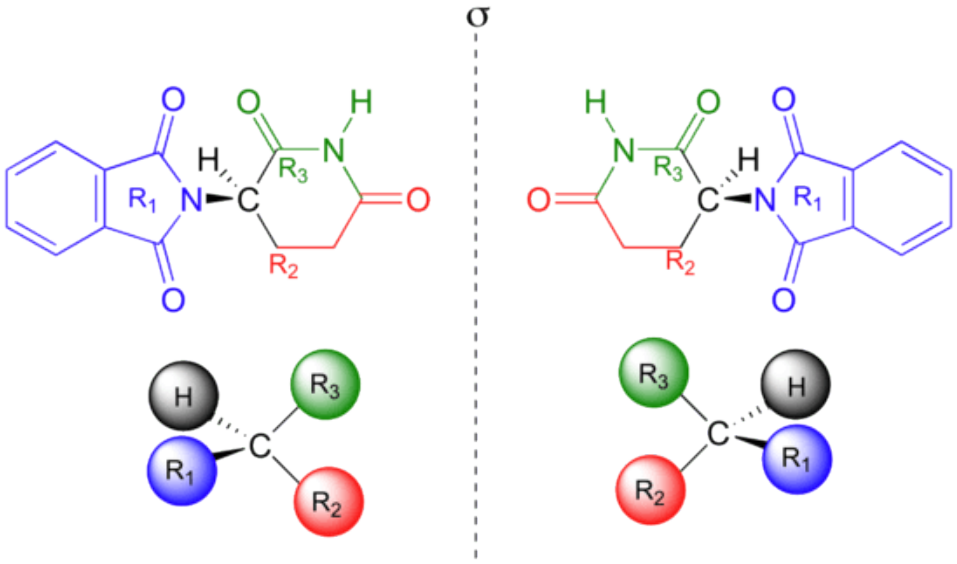


If you look carefully at the figure above, you will notice that molecule A and molecule B are mirror images of each other (the line labeled 's' represents a mirror plane). Furthermore, *they are not superimposable*: if we pick up molecule A, flip it around, and place it next to molecule B, we see that the two structures cannot be superimposed on each other. They are different molecules!



See a figure of the two enantiomers of the amino acid alanine

If you make models of the two stereoisomers of thalidomide and do the same thing, you will see that they too are mirror images, and cannot be superimposed (it well help to look at a color version of the figure below).



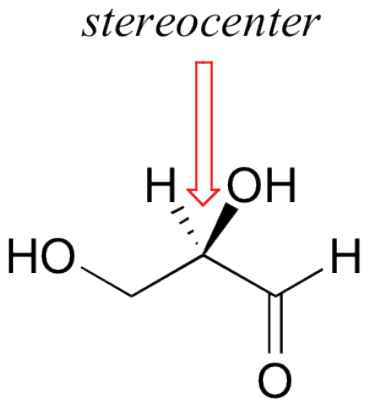
Thalidomide is a **chiral** molecule. Something is considered to be chiral if it cannot be superimposed on its own mirror image – in other words, if it is **asymmetric** (lacking in symmetry). The term 'chiral' is derived from the Greek word for 'handedness' – ie. right-handedness or left-handedness. Your hands are chiral: your right hand is a mirror image of your left hand, but if you place one hand on top of the other, both palms down, you see that they are not superimposable.

A pair of stereoisomers that are non-superimposable mirror images of one another are considered to have a specific type of stereoisomeric relationship – they are a pair of **enantiomers**. Thalidomide exists as a pair of enantiomers. On the macro level, your left and right hands are also a pair of enantiomers.

Naming Enantiomers: The R,S, System

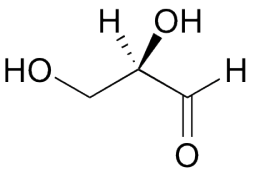
Chemists need to have a convenient way to distinguish between stereoisomers. The **Cahn-Ingold-Prelog system** is a set of rules that allows us to unambiguously define the stereochemical configuration of any stereocenter, using the designations '***R***' (from the Latin *rectus*, meaning right-handed) or '**S**' (from the Latin *sinister*, meaning left-handed).

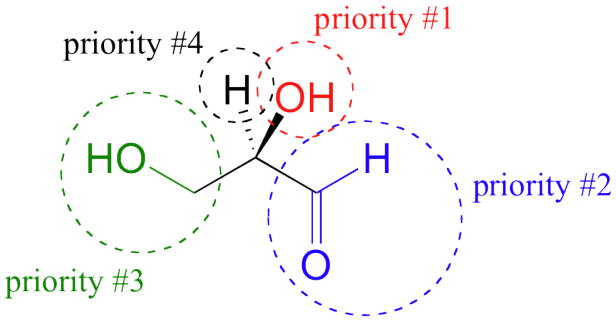
The rules for this system of stereochemical nomenclature are, on the surface, fairly simple. Because thalidomide is a somewhat complicated molecule, we'll use the simple 3-carbon sugar glyceraldehyde as our first example. You will want to make a model of the stereoisomer of glyceraldehyde shown below (be sure that you are making the correct enantiomer!).

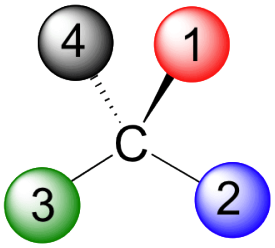


glyceraldehyde
(one enantiomer)

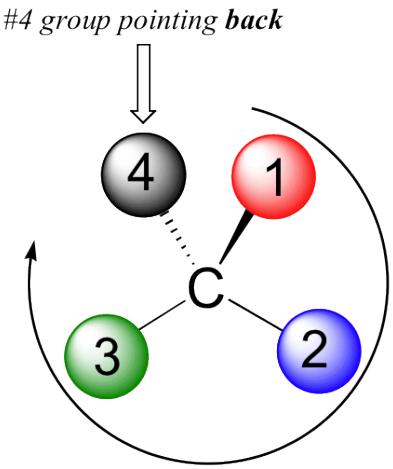
The first thing that we must do is to assign a **priority** to each of the four substituents bound to the **chiral carbon**. In this nomenclature system, the priorities are based on atomic number, with higher atomic numbers having a higher priority. We first look at the atoms that are directly bonded to the chiral carbon: these are H, O (in the hydroxyl), C (in the aldehyde), and C (in the CH_2OH group).



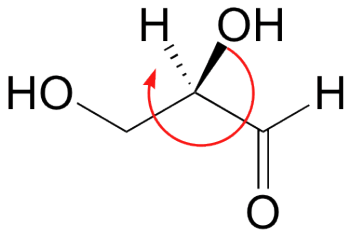




Two priorities are easy: hydrogen, with an atomic number of 1, is the lowest (#4) priority, and the hydroxyl oxygen, with atomic number 8, is priority #1. Carbon has an atomic number of 6. Which of the two 'C' groups is priority #2, the aldehyde or the CH_2OH? To determine this, we move one more bond away from the stereocenter: for the aldehyde we have a *double* bond to an oxygen, while on the CH_2OH group we have a *single* bond to an oxygen. If the atom is the same, double bonds have a higher priority than single bonds. Therefore, the aldehyde group is assigned #2 priority and the CH_2OH group the #3 priority. With our priorities assigned, we next make sure that the #4 priority group (the hydrogen) is pointed back away from ourselves, into the plane of the page (it is already).

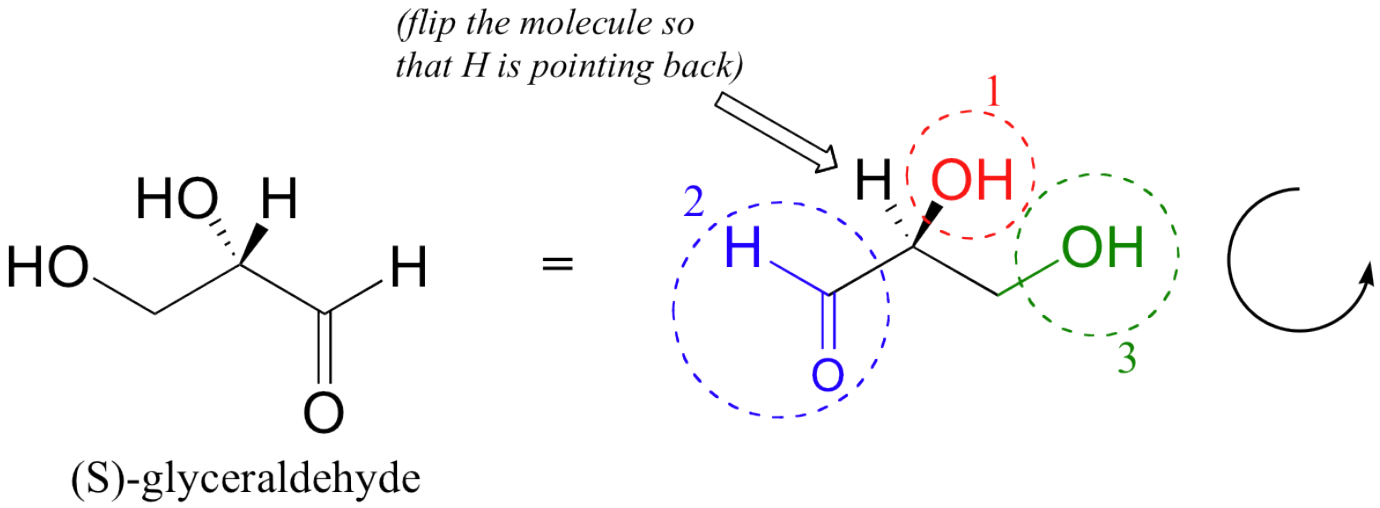


clockwise = R configuration



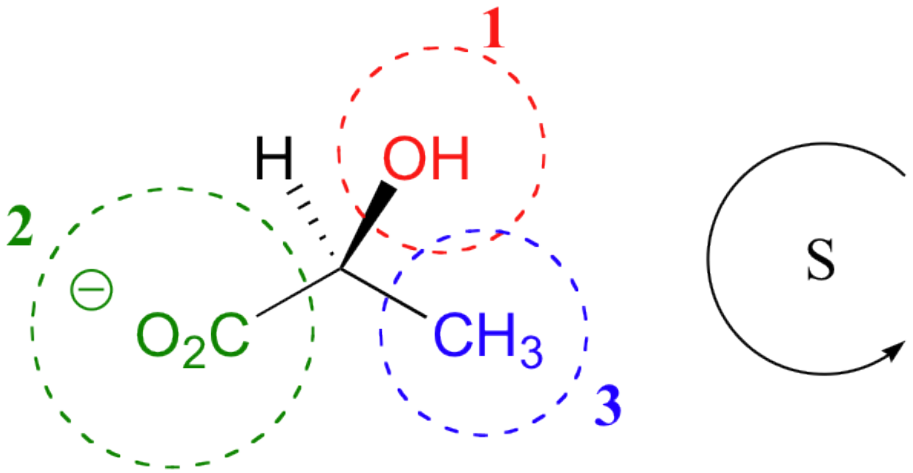
(R)-glyceraldehyde

Then, we trace a circle defined by the #1, #2, and #3 priority groups, in increasing order. For our glyceraldehyde example, this circle is clockwise, which tells us that this carbon has the 'R' configuration, and that this molecule is (R)-glyceraldehyde. For (S)-glyceraldehyde, the circle described by the #1, #2, and #3 priority groups is counter-clockwise (but first, we must flip the molecule over so that the H is pointing into the plane of the page).



(S)-glyceraldehyde

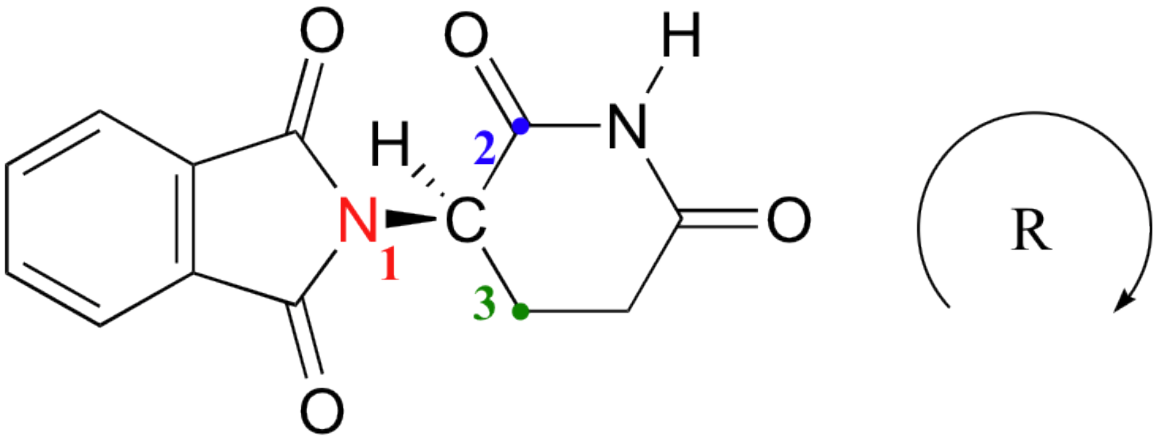
We can follow a similar procedure for a molecule such as lactate. Clearly, H is the #4 substituent and OH is #1. Owing to its three bonds to oxygen, the CO_2 group takes priority #2.



(S)-lactate

The structure shown is the S enantiomer of lactate.

Now, let's try to assign a stereochemical configuration to the enantiomer of thalidomide that is the effective medication. The #4 priority is again hydrogen (in fact, the #4 group will be hydrogen for most of the stereocenters we encounter). The nitrogen group is #1, the carbonyl side of the ring is #2, and the $-CH_2$ side of the ring is #3.



(R)-thalidomide

The hydrogen is shown pointing away from us, and the prioritized substituents trace a clockwise circle: this is the *R* enantiomer of thalidomide.

Example 26.4.2

Label stereochemistry for the figures of glyceraldehyde, alanine, lactate and amphetamine shown earlier in the chapter (section 3.3).

Example 26.4.3

Using solid or dashed wedges to show stereochemistry, draw the (R)-enantiomers of malate and ibuprofin (structures in exercise 3.6, this section), and mevalonate, 2-methylerithritol-4-phosphate, and dihydroorotate (structures in section 3.3).

Solutions

Summary

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 existance of these molecules are determined by concept known as **chirality**. The word "chiral" was derived from the Greek word for hand, because our hands display a good example of chirality since they are non-superimposable mirror images of each other.

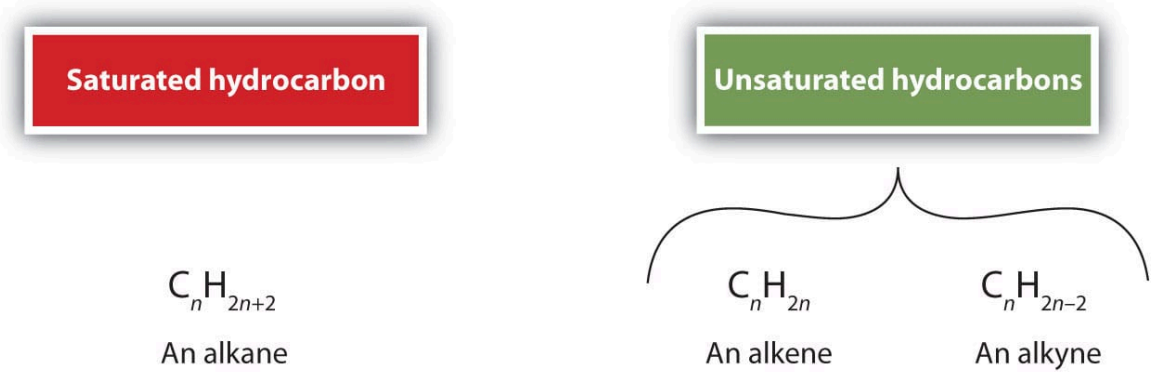
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- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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26.5: Alkenes and Alkynes

As noed 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:



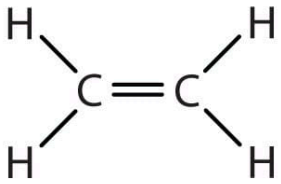
Alkenes

Some representative alkenes—their names, structures, and physical properties—are given in Table 26.5.1.

Table 26.5.1: 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 26.5.1. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbon atoms 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 26.5.1, ethene and propene, are most often called by their common names—ethylene and propylene,

respectively (Figure 26.5.1). 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.

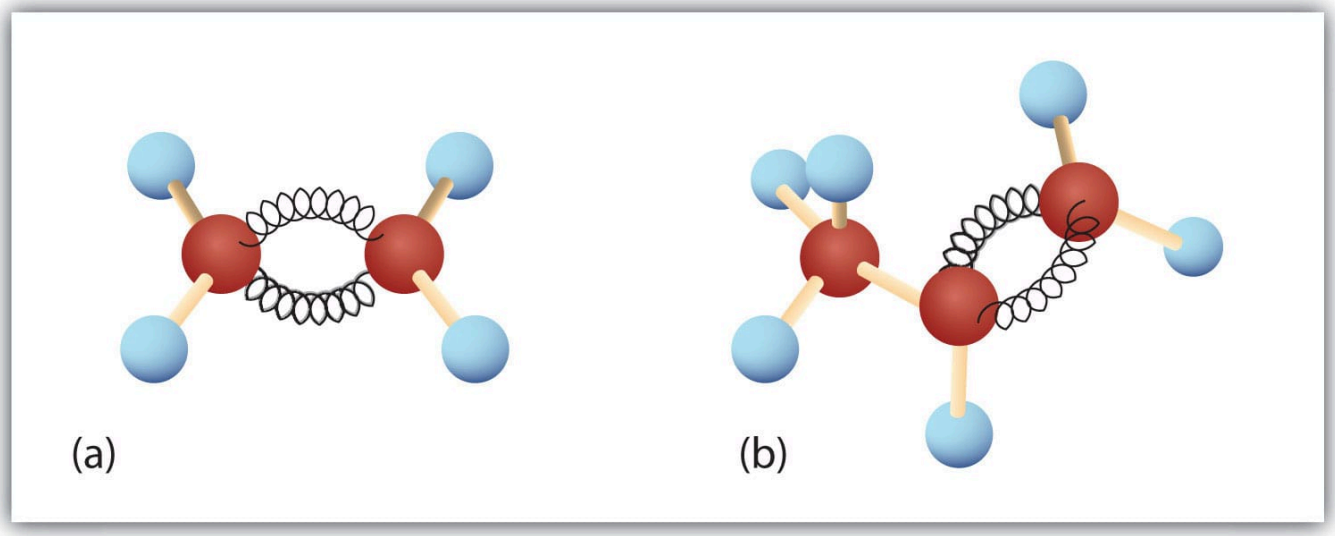


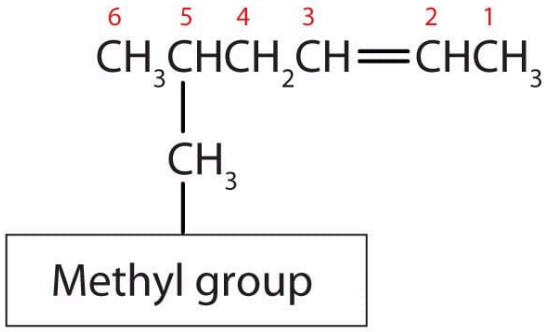
Figure 26.5.1: *Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.*

Note

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):

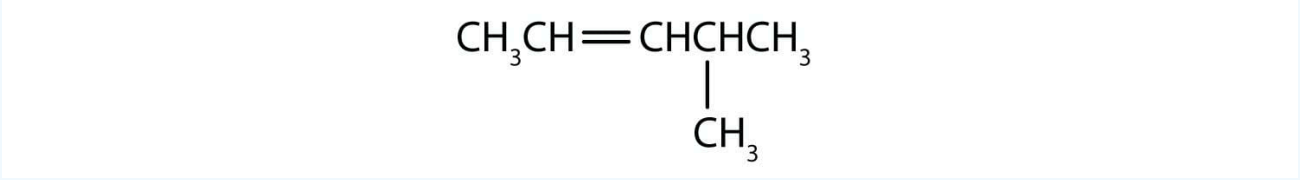
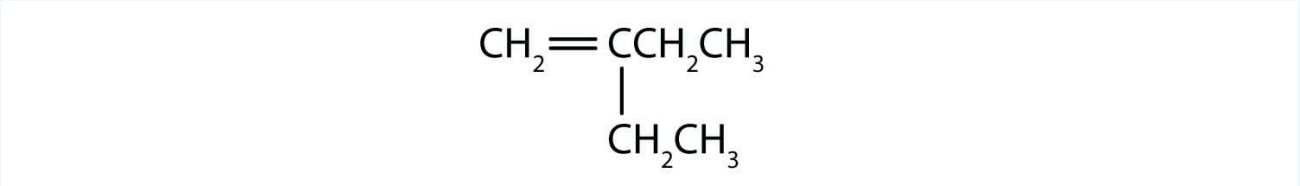
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound $CH_2{=}CHCH_3$ is *propene*.
2. If there are four or 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,



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 26.5.1

Name each compound.

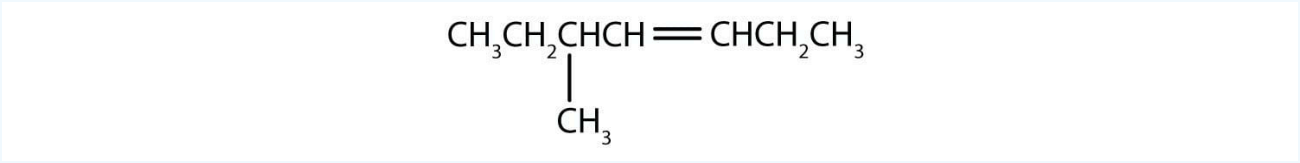
1. 
2. 

Solution

1. 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.
2. The longest chain containing the double bond has four carbon atoms, so the parent compound is a *butene* (rule 1). (The longest chain overall has five carbon atoms, but it does not contain the double bond, so the parent name is not *pentene*.) 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 1-butene. There is an ethyl group on the second carbon atom (rule 3), so the compound's name is 2-ethyl-1-butene.

Exercise 26.5.1

Name each compound.

1. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$
2. 

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.

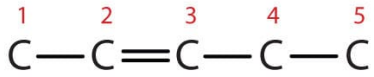
Example 26.5.2

Draw the structure for each compound.

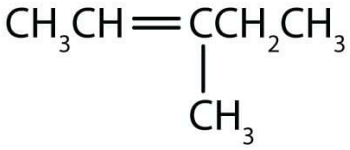
1. 3-methyl-2-pentene
2. cyclohexene

Solution

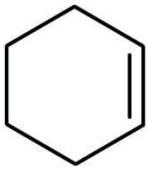
1. First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:



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.



2. 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 26.5.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

Steroisomerism in Alkenes

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure 26.5.2.

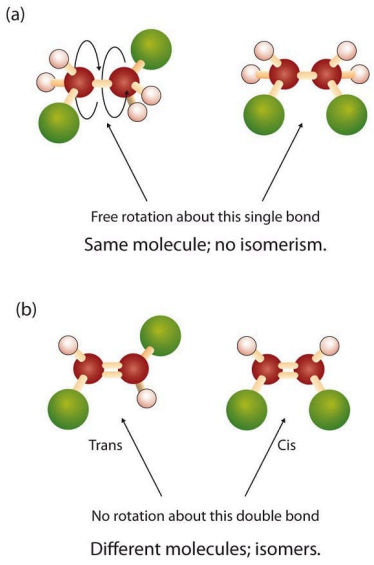


Table 26.5.2*: Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.*

In 1,2-dichloroethane (part (a) of Figure 26.5.2), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:



In 1,2-dichloroethene (part (b) of Figure 26.5.2), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the cis isomer (Latin *cis*, meaning "on this side") and is named cis-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the trans isomer (Latin *trans*, meaning "across") and is named *trans*-1,2-dichloroethene. These two compounds are cis-trans isomers (or geometric isomers), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $CH_3CH{=}CHCH_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in cis-trans isomerism (Figure 26.5.3).

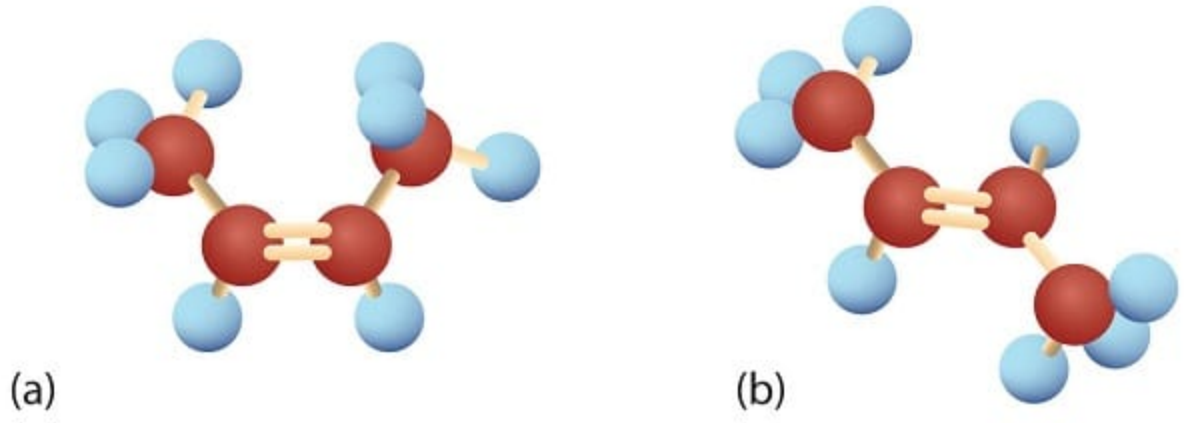
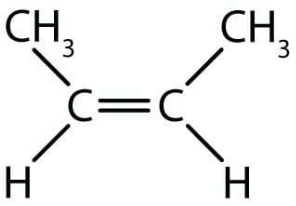
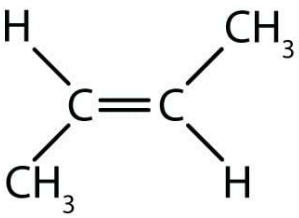


Table 26.5.3*: Ball-and-Spring Models of (a) Cis-2-Butene and (b) Trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.*

Cis-2-butene has both methyl groups on the same side of the molecule. *Trans*-2-butene has the methyl groups on opposite sides of the molecule. Their structural formulas are as follows:

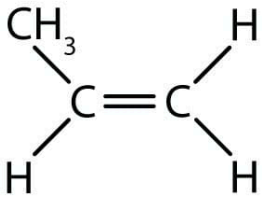


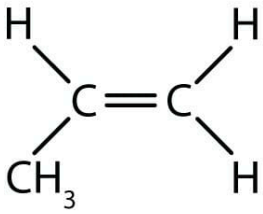
cis-2-butene



trans-2-butene

Note, however, that the presence of a double bond does not necessarily lead to cis-trans isomerism. We can draw two *seemingly* different propenes:





However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

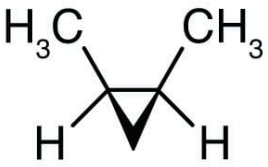
1. Rotation must be restricted in the molecule.
2. There must be two nonidentical groups on *each* doubly bonded carbon atom.

In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

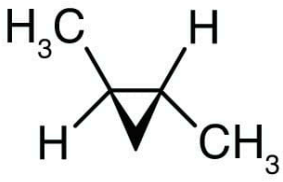
- Alkenes with a $C{=}CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C{=}CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.

- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon–carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring.



Cis-1,2-dimethylcyclopropane



Trans-1,2-dimethylcyclopropane

Example 26.5.3

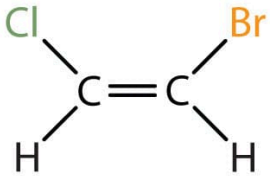
Which compounds can exist as cis-trans (geometric) isomers? Draw them.

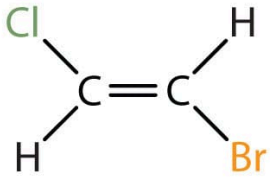
1. $CHCl=CHBr$
2. $CH_2=CBrCH_3$
3. $(CH_3)_2C=CHCH_2CH_3$
4. $CH_3CH=CHCH_2CH_3$

Solution

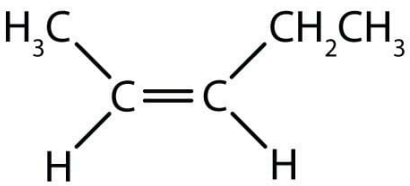
All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

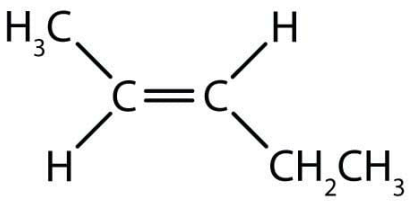
1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:





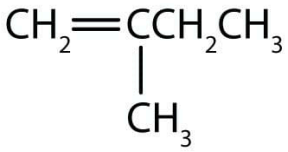
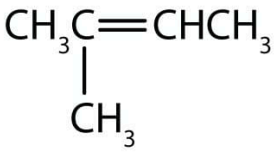
2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl (CH_3) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:





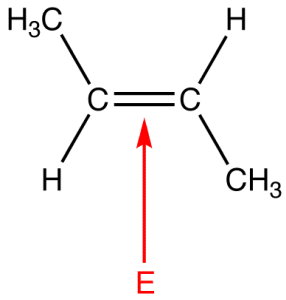
Exercise 26.5.3

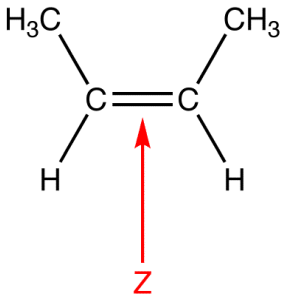
Which compounds can exist as cis-trans isomers? Draw them.

a. $CH_2=CHCH_2CH_2CH_3$
b. $CH_3CH=CHCH_2CH_3$
c. $CH_3CH_2CH=CHCH_2CH_3$
d. 
e. 

E,Z Convention

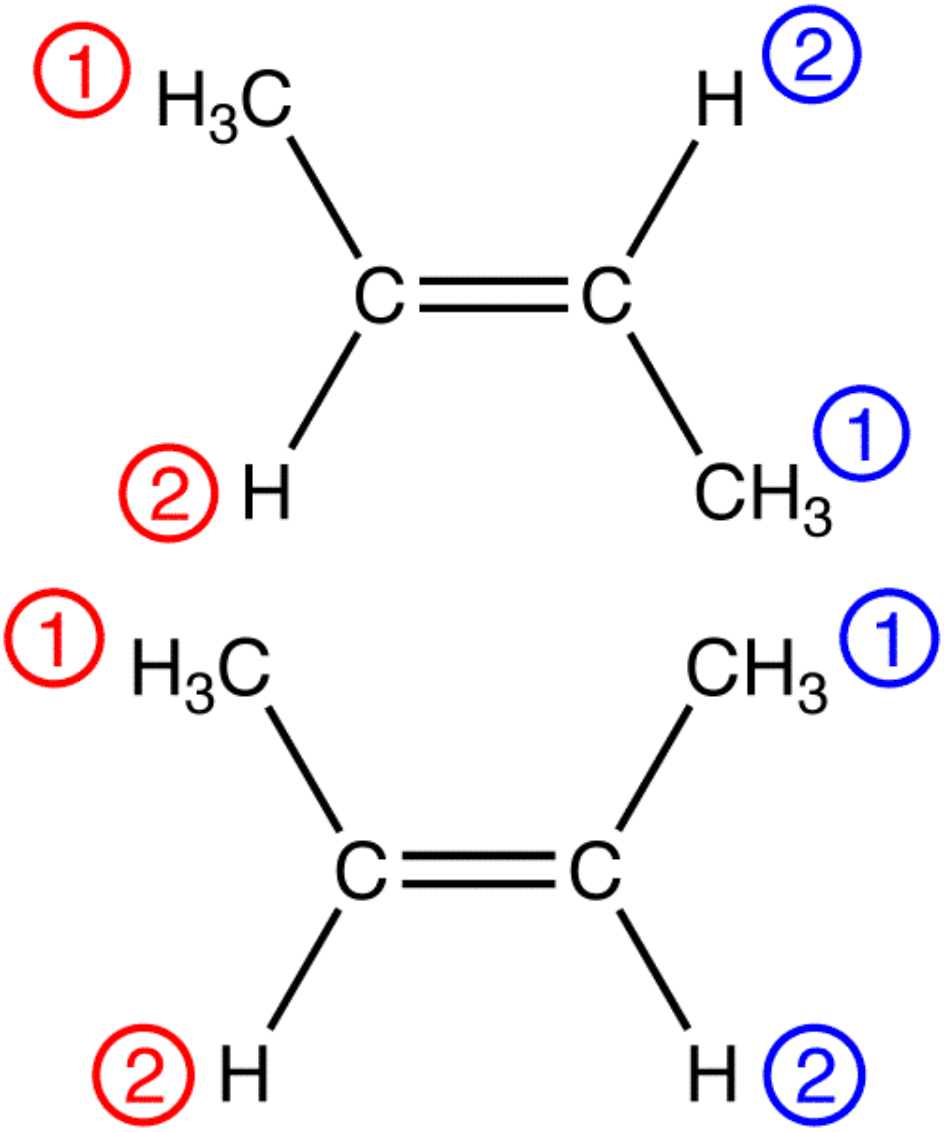
E,Z Convention is a method used to specify relative configuration at carbon atoms in alkene groups. According to E,Z convention, if the pair of carbon atoms in an alkene group could exist in two relative configurations, one is designated using the label E and the other the label Z.





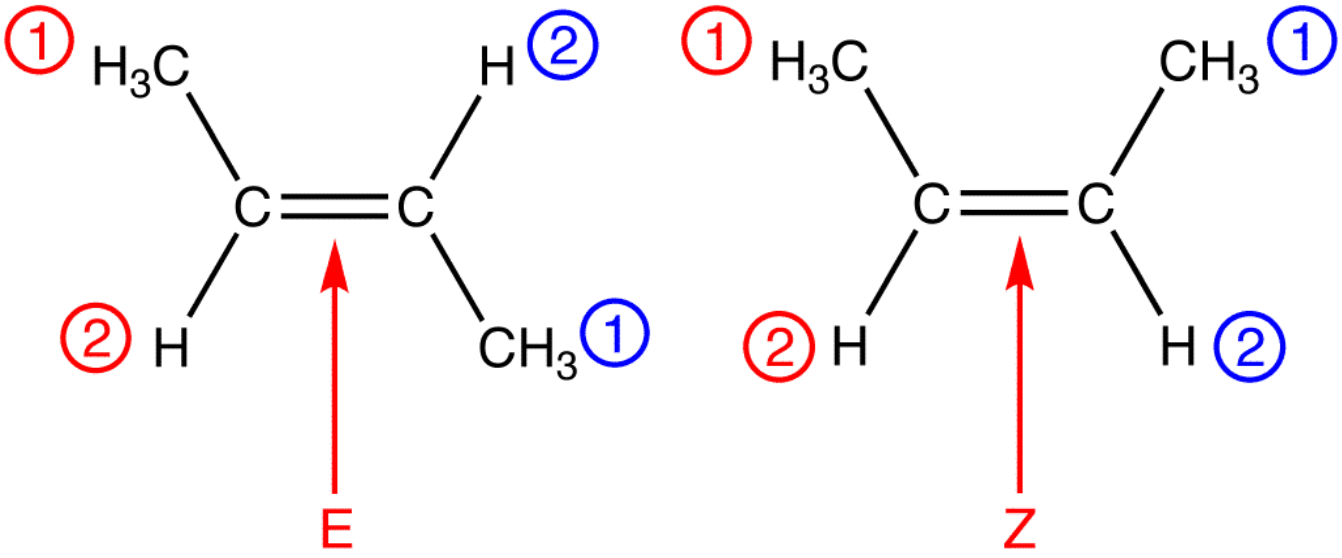
To determine whether an alkene group is E or Z, use the following two-step procedure.

Step 1: Assign priority numbers to the two ligands on each carbon atom in the alkene group. (See R,S convention for the procedure.)



Step 2:

like-numbered ligands	relative configuration
same side of double bond	Z
opposite side of double bond	E



Alkynes

The simplest alkyne—a hydrocarbon with carbon-to-carbon triple bond—has the molecular formula C_2H_2 and is known by its common name—acetylene (Figure 26.5.1). Its structure is H–C≡C–H.

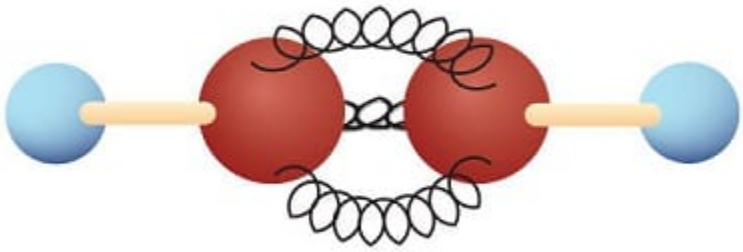


Figure 26.5.4: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

Note

Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Alkynes are similar to alkenes in both physical and chemical properties. For example, alkynes undergo many of the typical addition reactions of alkenes. The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *-yne* rather than *-ene*. The IUPAC name for acetylene is ethyne. The names of other alkynes are illustrated in the following exercises.

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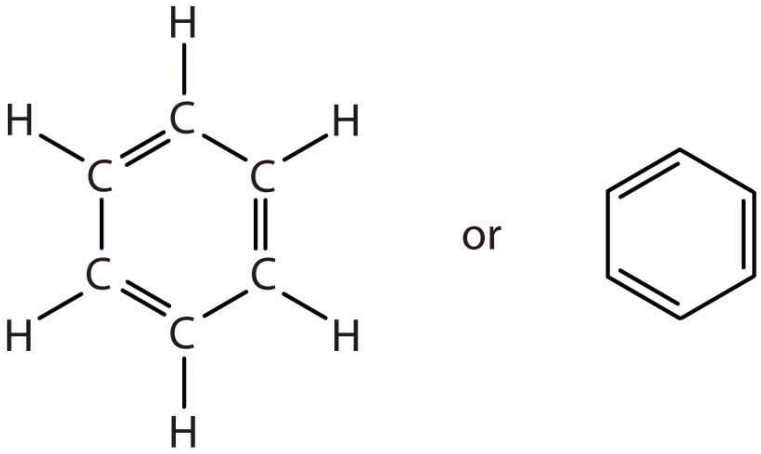
26.6: Aromatic Hydrocarbons

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance. The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14}—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Note

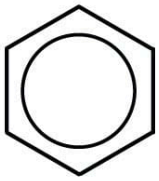
Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable.

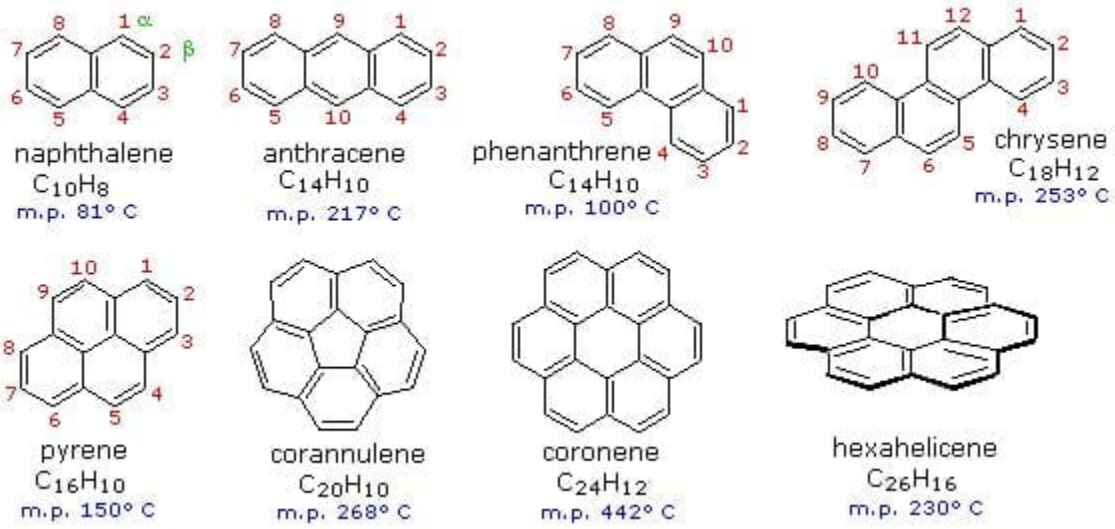
Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

Benzene rings may be joined together (fused) to give larger polycyclic aromatic compounds. A few examples are drawn below, together with the approved numbering scheme for substituted derivatives. The peripheral carbon atoms (numbered in all but the last three examples) are all bonded to hydrogen atoms. Unlike benzene, all the C-C bond lengths in these fused ring aromatics are not the same, and there is some localization of the pi-electrons.

The six benzene rings in coronene are fused in a planar ring; whereas the six rings in hexahelicene are not joined in a larger ring, but assume a helical turn, due to the crowding together of the terminal ring atoms. This helical configuration renders the hexahelicene molecule chiral, and it has been resolved into stable enantiomers.



Aromaticity

Aromaticity is a property of conjugated cycloalkenes in which the stabilization of the molecule is enhanced due to the ability of the electrons in the orbitals to delocalize. This act as a framework to create a planar molecule. Why do we care if a compound is aromatic or not? Because we encounter aromatics every single day of our lives. Without aromatic compounds, we would not only be lacking many material necessities, our bodies would also not be able to function. Aromatic compounds are essential in industry; about 35 million tons of aromatic compounds are produced in the world every year to produce important chemicals and polymers, such as polyester and nylon. Aromatic compounds are also vital to the biochemistry of all living things. Three of the twenty amino acids used to form proteins ("the building blocks of life") are aromatic compounds and all five of the nucleotides that make up DNA and RNA sequences are all aromatic compounds. Needless to say, aromatic compounds are vital to us in many aspects.

The three general requirements for a compound to be aromatic are:

1. The compound must be cyclic
2. Each element within the ring must have a p-orbital that is *perpendicular* to the ring, hence the molecule is planar.
3. The compound must follow Hückel's Rule (the ring has to contain 4n+2 p-orbital electrons).

Among the many distinctive features of benzene, its aromaticity is the major contributor to why it is so unreactive. This section will try to clarify the theory of aromaticity and why aromaticity gives unique qualities that make these conjugated alkenes inert to compounds such as Br_2 and even hydrochloric acid. It will also go into detail about the unusually large resonance energy due to the six conjugated carbons of benzene.

dd.bmp

The delocalization of the p-orbital carbons on the sp^2 hybridized carbons is what gives the aromatic qualities of benzene.

Benzene Structure (1).bmp

Because of the aromaticity of benzene, the resulting molecule is planar in shape with each C-C bond being 1.39 Å in length and each bond angle being 120°. You might ask yourselves how it's possible to have all of the bonds to be the same length if the ring is conjugated with both single (1.47 Å) and double (1.34 Å), but it is important to note that there are no distinct single or double bonds within the benzene. Rather, the delocalization of the ring makes each count as one and a half bonds between the carbons which makes sense because experimentally we find that the actual bond length is somewhere in between a single and double bond. Finally, there are a total of six p-orbital electrons that form the stabilizing electron clouds above and below the aromatic ring.

Aromatic Hydrocarbon Nomenclature

In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure 26.6.1 shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent.

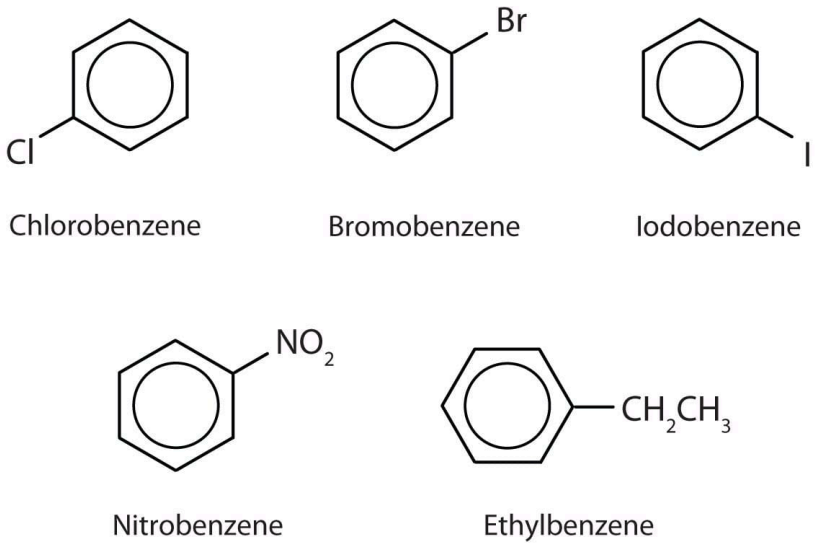
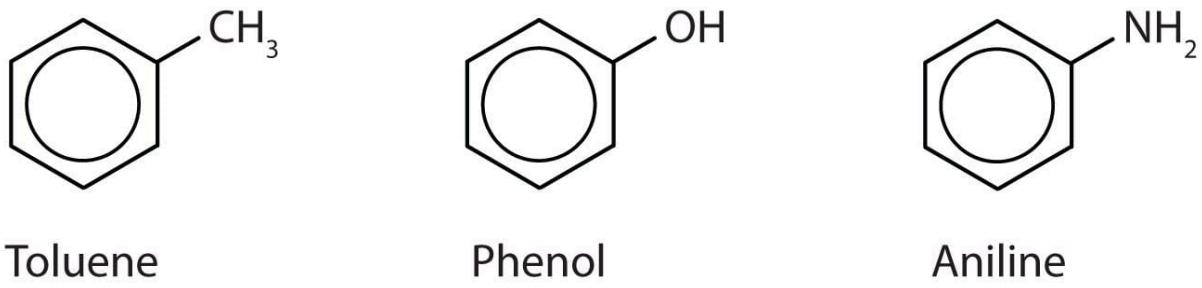


Figure 26.6.1: Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, NO_2 as nitro, and CH_3CH_2 as ethyl.

Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table 26.6.1.



When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative

positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure 26.6.2). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path.

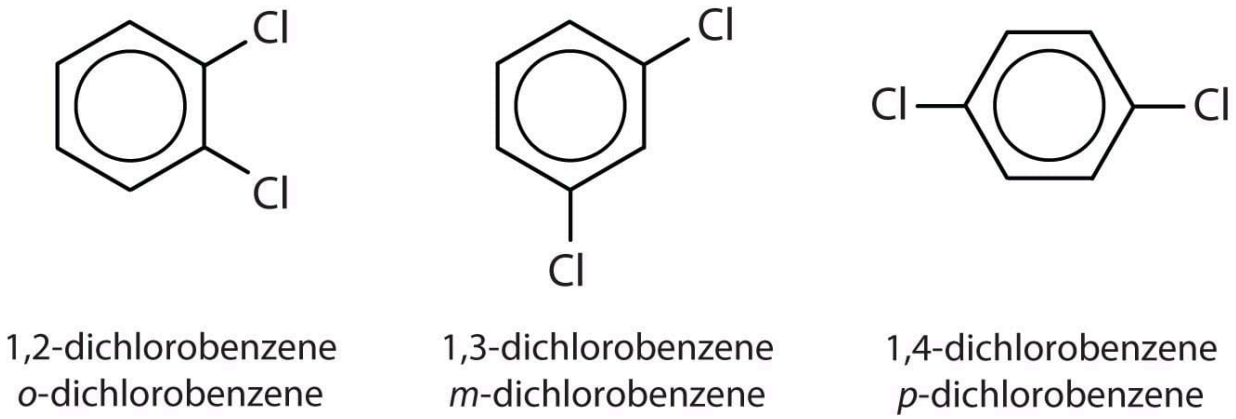
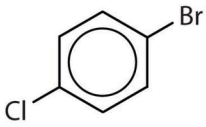
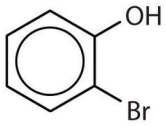


Figure 26.6.2: *The Three Isomeric Dichlorobenzenes*

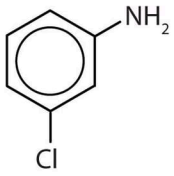
In Figure 26.6.2, common names are also used: the prefix *ortho* (*o*-) for 1,2-disubstitution, *meta* (*m*-) for 1,3-disubstitution, and *para* (*p*-) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1:



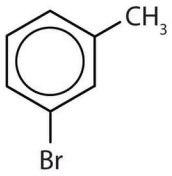
1-Bromo-4-chlorobenzene
p-Bromochlorobenzene



2-Bromophenol
o-Bromophenol



3-Chloroaniline
m-Chloroaniline

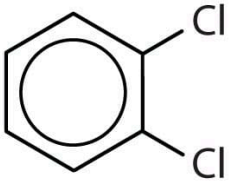


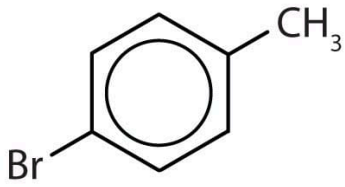
3-Bromotoluene
m-Bromotoluene

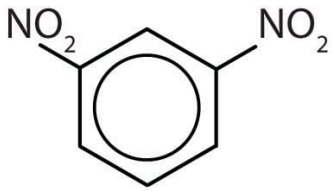
Example 26.6.2

Name each compound using both the common name and the IUPAC name.

1.



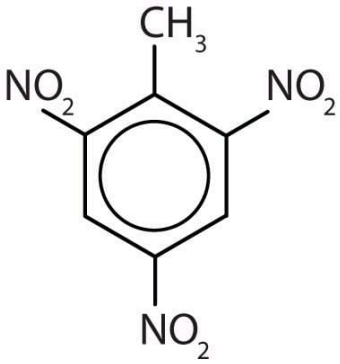
2. 

3. 

Solution

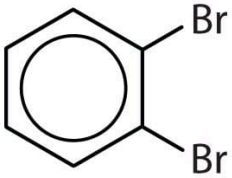
1. The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene or 1,2-dichlorobenzene.
2. The benzene ring has a methyl (CH_3) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.
3. The benzene ring has two nitro (NO_2) groups in the first and third positions. It is *m*-dinitrobenzene or 1,3-dinitrobenzene.

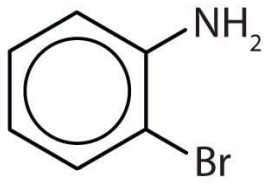
Note: The nitro (NO_2) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).

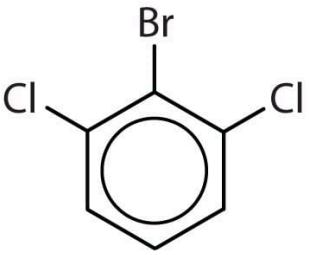


Exercise 26.6.2

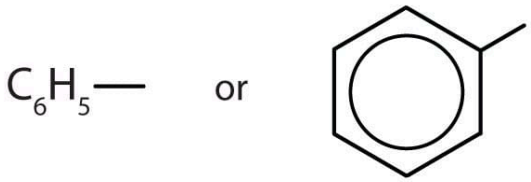
Name each compound using both the common name and the IUPAC name.

1. 

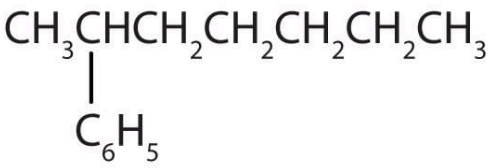
2. 

3. 

Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene (C_6H_6) by removing one hydrogen atom (C_6H_5) and is called a *phenyl* group, from *pheno*, an old name for benzene.



Phenyl group



2-Phenylheptane

Contributors and Attributions

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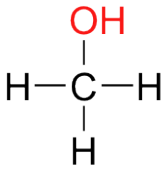
26.7: Organic Compounds Containing Functional Groups

Functional groups are atoms or small groups of atoms (two to four) that exhibit a characteristic reactivity. A particular functional group will almost always display its characteristic chemical behavior when it is present in a compound. Because of their importance in understanding organic chemistry, functional groups have characteristic names that often carry over in the naming of individual compounds incorporating specific groups

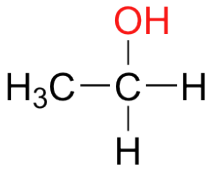
As we progress in our study of organic chemistry, it will become extremely important to be able to quickly recognize the most common functional groups, because they are the key structural elements that define how organic molecules react. For now, we will only worry about drawing and recognizing each functional group, as depicted by Lewis and line structures. Much of the remainder of your study of organic chemistry will be taken up with learning about how the different functional groups tend to behave in organic reactions.

Alcohols and Phenols

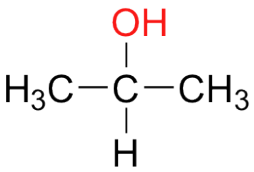
We have already seen the simplest possible example of an **alcohol** functional group in methanol. In the alcohol functional group, a carbon is single-bonded to an OH group (this OH group, by itself, is referred to as a **hydroxyl**). If the central carbon in an alcohol is bonded to only one other carbon, we call the group a primary alcohol. In secondary alcohols and tertiary alcohols, the central carbon is bonded to two and three carbons, respectively. Methanol, of course, is in class by itself in this respect.



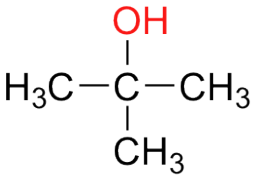
methanol



a primary alcohol



a secondary alcohol

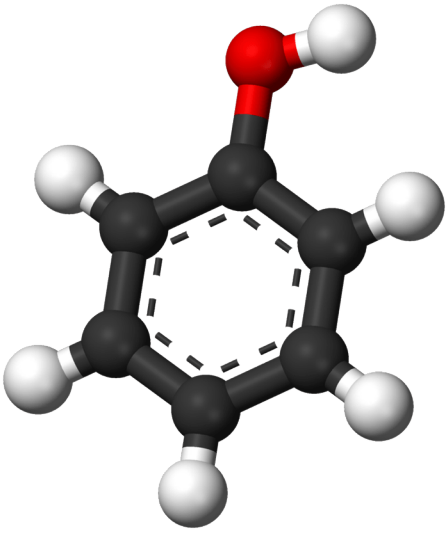


a tertiary alcohol

Compounds in which an OH group is attached directly to an aromatic ring are designated ArOH and called phenols. Phenols differ from alcohols in that they are slightly acidic in water. They react with aqueous sodium hydroxide (NaOH) to form salts.

$$ArOH_{(aq)} + NaOH_{(aq)} \rightarrow ArONa_{(aq)} + H_2O \tag{26.7.1}$$

The parent compound, C_6H_5OH, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive (“hospital smell”) odor.





(Left) Structure of Phenol (right) Approximately two grams of phenol in glass vial. Image used with permisison from Wikipedia

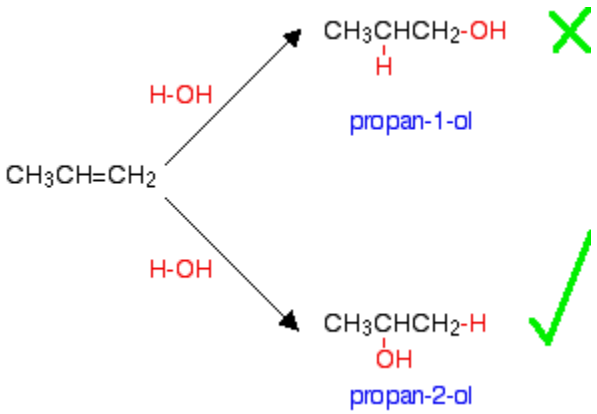
Preparation and Uses of Alcohols

There are two primary methods to make alcohols in the laboratory: Hydration of an alkene and hydrolysis of an alkyl halide.

Ethanol is manufactured by reacting ethene with steam. The catalyst used is solid silicon dioxide coated with phosphoric(V) acid. The reaction is reversible.

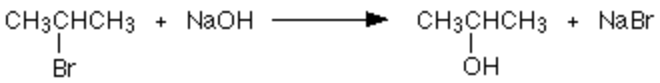
$$CH_2{=}CH_{2(g)} + H_2O_{(g)} \underset{}{\overset{H_3PO_4}{\rightleftharpoons}} CH_3CH_2OH_{(g)}$$

Some - but not all - other alcohols can be made by similar reactions. The catalyst used and the reaction conditions will vary from alcohol to alcohol. The reason that there is a problem with some alcohols is well illustrated with trying to make an alcohol from propene, $CH_3CH{=}CH_2$. In principle, there are two different alcohols which might be formed:

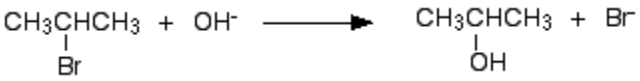


You might expect to get either propan-1-ol or propan-2-ol depending on which way around the water adds to the double bond. In practice what you get is propan-2-ol. If you add a molecule H-X across a carbon-carbon double bond, the hydrogen nearly always gets attached to the carbon with the most hydrogens on it already - in this case the CH2 rather than the CH. The effect of this is that there are bound to be some alcohols which it is impossible to make by reacting alkenes with steam because the addition would be the wrong way around.

The other common method to make alcholes is a substitution reaction, the halogen atom is replaced by an -OH group to give an alcohol. For example:



Or, as an ionic equation:



In this example, 2-bromopropane is converted into propan-2-ol. The halogenoalkane is heated under reflux with a solution of sodium or potassium hydroxide. Heating under reflux means heating with a condenser placed vertically in the flask to prevent loss of volatile substances from the mixture.

The solvent is usually a 50/50 mixture of ethanol and water, because everything will dissolve in that. The halogenoalkane is insoluble in water. If you used water alone as the solvent, the halogenoalkane and the sodium hydroxide solution wouldn't mix and the reaction could only happen where the two layers met.

Ethanol is usually sold as industrial methylated spirits, which is ethanol with a small quantity of methanol and possibly some color added. Because methanol is poisonous, industrial methylated spirits are unfit to drink, allowing purchasers to avoid the high taxes levied on alcoholic drinks. Ethanol burns to produce carbon dioxide and water, as shown in the equation below, and can be used as a fuel in its own right or in mixtures with petrol (gasoline). "Gasohol" is a petrol/ethanol mixture containing approximately 10–20% ethanol. Because ethanol can be produced by fermentation, this is a useful method for countries without an oil industry to reduce the amount of petrol imports.

$$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \tag{26.7.2}$$

Ethanol is widely used as a solvent. It is relatively safe and can be used to dissolve many organic compounds that are insoluble in water. It is used, for example, in many perfumes and cosmetics.

Methanol also burns to form carbon dioxide and water:

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O \tag{26.7.3}$$

It can be used a a petrol additive to improve combustion, and its use as a fuel in its own right is under investigation. Furthremore, most methanol is used to make other compounds, for example, methanal (formaldehyde), ethanoic acid, and methyl esters of various acids. In most cases, these are then converted into further products.

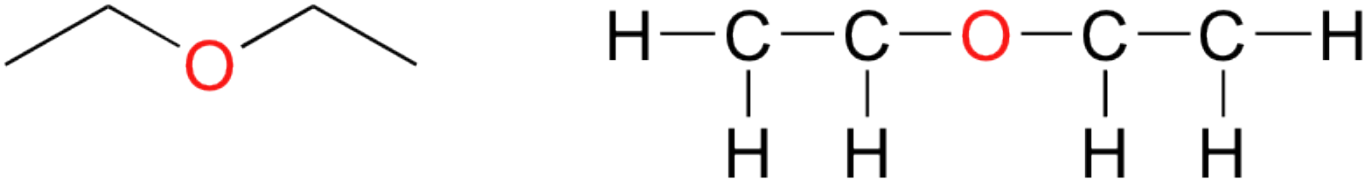
Phenols are widely used as antiseptics (substances that kill microorganisms on living tissue) and as disinfectants (substances intended to kill microorganisms on inanimate objects such as furniture or floors). The first widely used antiseptic was phenol. Joseph Lister used it for antiseptic surgery in 1867. Phenol is toxic to humans, however, and can cause severe burns when applied to the skin. In the bloodstream, it is a systemic poison—that is, one that is carried to and affects all parts of the body. Its severe side effects led to searches for safer antiseptics, a number of which have been found.



An operation in 1753, painted by Gaspare Traversi, of a surgery before antiseptics were used.

Ethers

In an **ether** functional group, a central oxygen is bonded to two carbons. Below are the line and Lewis structures of diethyl ether, a common laboratory solvent and also one of the first medical anaesthesia agents.

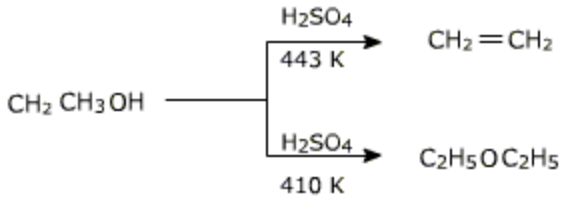


Preparation and Uses of Ethers

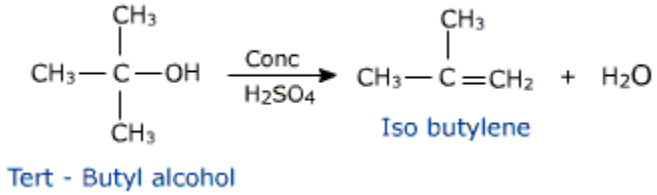
Acid-catalyzed dehydration of small 1°-alcohols constitutes a specialized method of preparing symmetrical ethers. As shown in the following two equations, the success of this procedure depends on the temperature. At 110° to 130 °C an S_N2 reaction of the alcohol conjugate acid leads to an ether product. At higher temperatures (over 150 °C) an E2 elimination takes place.

2 CH_3CH_2-OH + H_2SO_4	130 °C ⟶	CH_3CH_2-O-CH_2CH_3 + H_2O
CH_3CH_2-OH + H_2SO_4	150 °C ⟶	CH_2=CH_2 + H_2O

In this reaction alcohol has to be used in excess and the temperature has to be maintained around 413 K. If alcohol is not used in excess or the temperature is higher, the alcohol will preferably undergo dehydration to yield alkene.



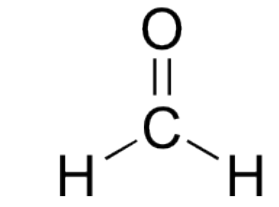
If ethanol is dehydrated to ethene in presence of sulfuric acid at 433 K but as 410 K, ethoxyethane is the main product. The dehydration of secondary and tertiary alcohols to get corresponding ethers is unsuccessful as alkenes are formed easily in these reactions.



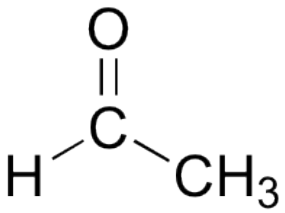
This reaction **cannot** be employed to prepare unsymmetrical ethers. It is because a mixture of products is likely to be obtained.

Aldehydes and Ketones

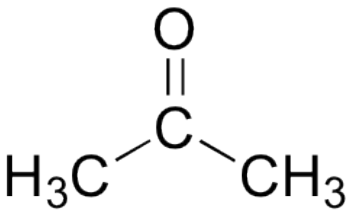
There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded 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



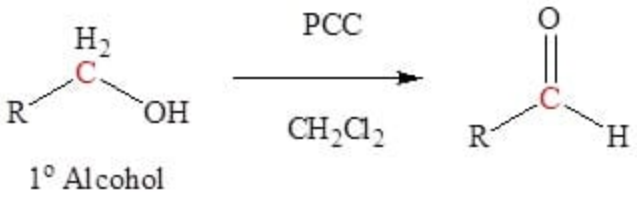
acetaldehyde



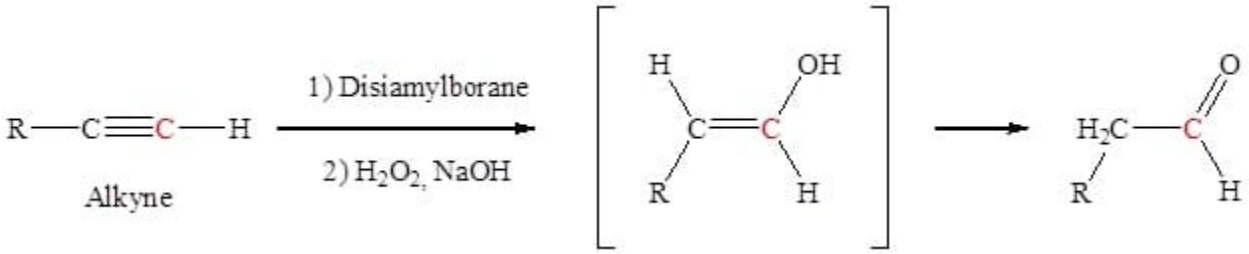
acetone
(a ketone)

Preparation and Uses of Aldehydes and Ketones

Aldehydes and ketones can be prepared using a wide variety of reactions. Although these reactions are discussed in greater detail in other sections, they are listed here as a summary and to help with planning multistep synthetic pathways. A common way to synthesize aldehydes is the ixidation of 1° alcohols to form aldehydes

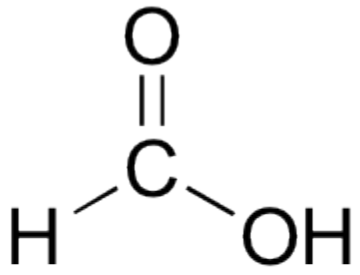


Hydration of an alkyne to form aldehydes via an addition reaction of a hydroxyl group to an alkyne forms an aldehyde. The addition of a hydroxyl group to an alkyne causes tautomerization which subsequently forms a carbonyl.

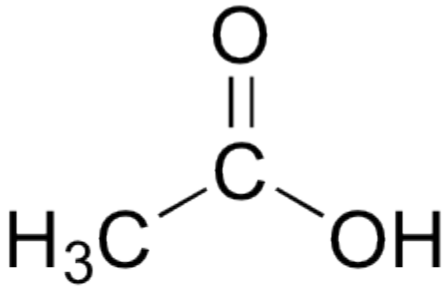


Carboxylic acids

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.

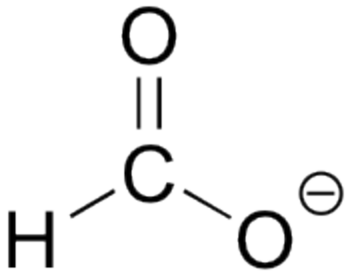


formic acid

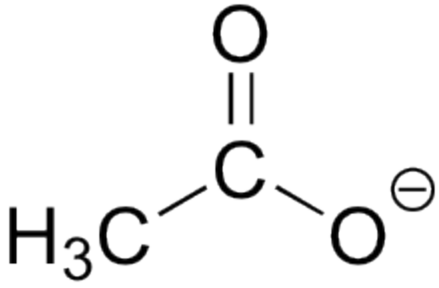


acetic acid (vinegar)

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!).



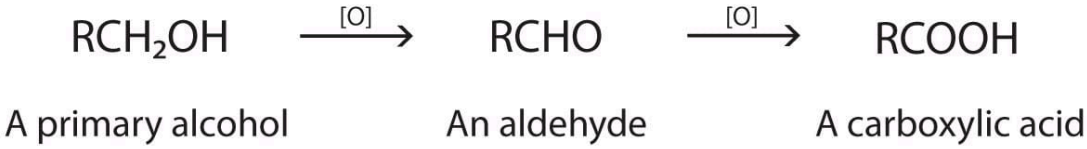
formate



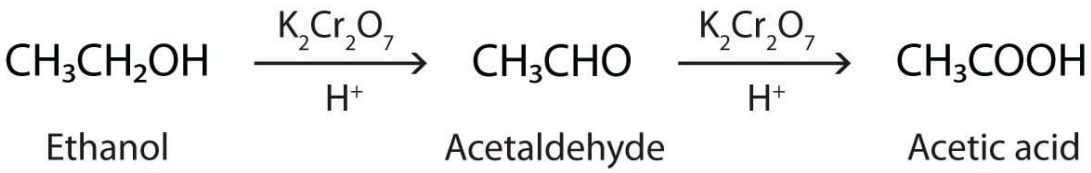
acetate

Preparation and Uses of Carboxylic Acids

The oxidation of aldehydes or primary alcohols forms carboxylic acids:



In the presence of an oxidizing agent, ethanol is oxidized to acetaldehyde, which is then oxidized to acetic acid.



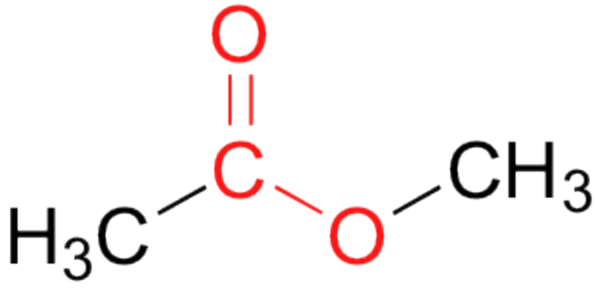
This process also occurs in the liver, where enzymes catalyze the oxidation of ethanol to acetic acid.

$$\mathrm{CH_3CH_2OH} \xrightarrow[\text{oxidizing agent}]{\text{alcohol dehydrogenase}} \mathrm{CH_3CHO} \xrightarrow[\text{oxidizing agent}]{\text{alcohol dehydrogenase}} \mathrm{CH_3COOH\%}$$

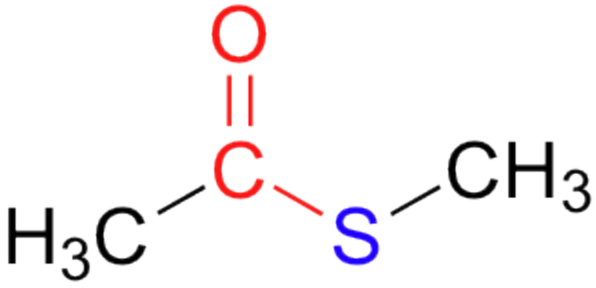
Acetic acid can be further oxidized to carbon dioxide and water.

Esters

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.



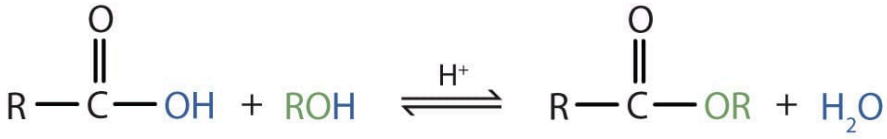
an ester



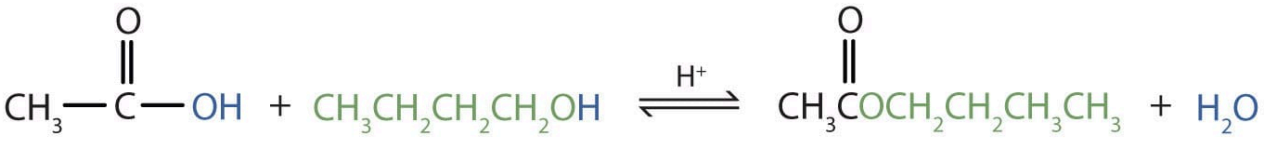
a thioester

Preparation and Uses of Esters

Some esters can be prepared by esterification, a reaction in which a carboxylic acid and an alcohol, heated in the presence of a mineral acid catalyst, form an ester and water:



The reaction is reversible. As a specific example of an esterification reaction, butyl acetate can be made from acetic acid and 1-butanol.

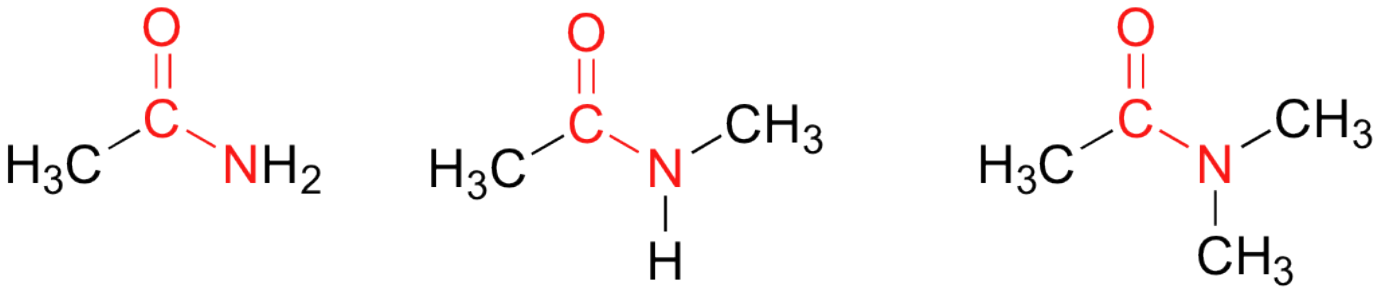


Acetic acid 1-Butanol Butyl acetate

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer “dries,” leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

Amides

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.



Preparation and Uses of Amides

The addition of ammonia (NH_3) to a carboxylic acid forms an amide, but the reaction is very slow in the laboratory at room temperature. Water molecules are split out, and a bond is formed between the nitrogen atom and the carbonyl carbon atom.

$$CH_3COOH + NH_3 \longrightarrow CH_3CONH_2 + H_2O$$

Acetic acid → Acetamide

In living cells, amide formation is catalyzed by enzymes. Proteins are polyamides; they are formed by joining amino acids into long chains. In proteins, the amide functional group is called a *peptide bond*.

With the exception of formamide ($HCONH_2$), which is a liquid, all simple amides are solids (Table 26.7.1). The lower members of the series are soluble in water, with borderline solubility occurring in those that have five or six carbon atoms. Like the esters, solutions of amides in water usually are neutral—neither acidic nor basic.

Table 26.7.1: Physical Constants of Some Unsubstituted Amides

Condensed Structural Formula	Name	Melting Point (°C)	Boiling Point (°C)	Solubility in Water
$HCONH_2$	formamide	2	193	soluble
CH_3CONH_2	acetamide	82	222	soluble
$CH_3CH_2CONH_2$	propionamide	81	213	soluble
$CH_3CH_2CH_2CONH_2$	butyramide	115	216	soluble
$C_6H_5CONH_2$	benzamide	132	290	slightly soluble

The amides generally have high boiling points and melting points. These characteristics and their solubility in water result from the polar nature of the amide group and hydrogen bonding (Figure 26.7.1). (Similar hydrogen bonding plays a critical role in determining the structure and properties of proteins, deoxyribonucleic acid [DNA], ribonucleic acid [RNA], and other giant molecules so important to life processes.

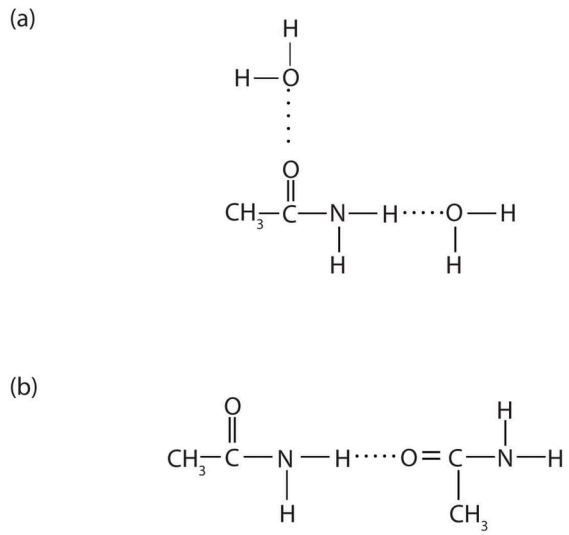
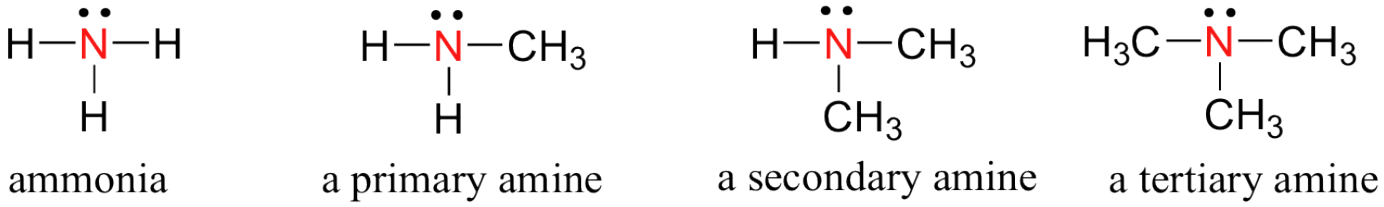


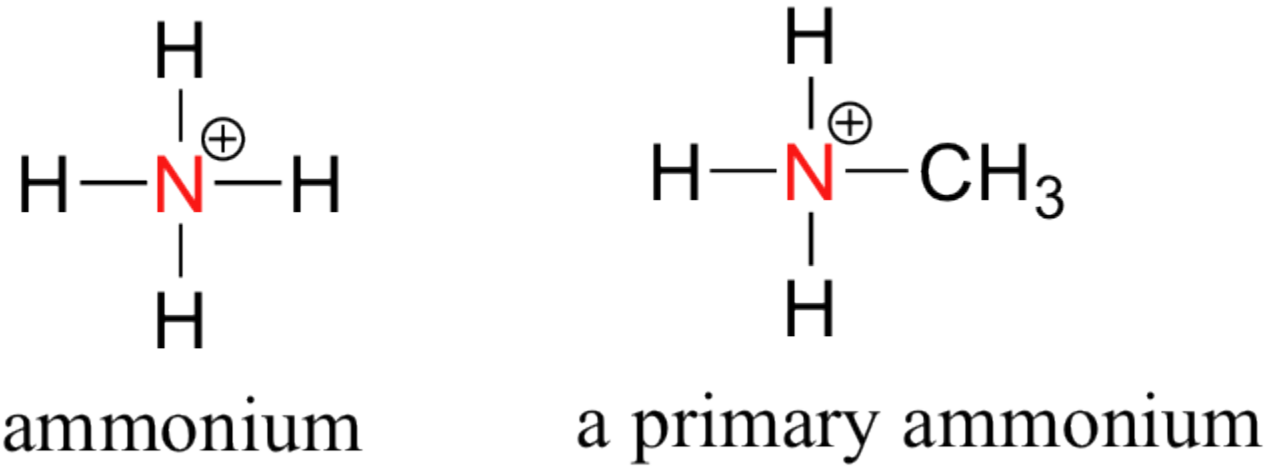
Figure 26.7.1: *Hydrogen Bonding in Amides. Amide molecules can engage in hydrogen bonding with water molecules (a). Those amides with a hydrogen atom on the nitrogen atom can also engage in hydrogen bonding (b). Both hydrogen bonding networks extend in all directions.*

Amines

Ammonia is the simplest example of a functional group called **amines**. Just as there are primary, secondary, and tertiary alcohols, there are primary, secondary, and tertiary amines.



One of the most important properties of amines is that they are basic, and are readily protonated to form **ammonium** cations.



Preparation and Uses of Amines

The halogenoalkane is heated with a concentrated solution of ammonia in ethanol. The reaction is carried out in a sealed tube. You couldn't heat this mixture under reflux, because the ammonia would simply escape up the condenser as a gas. We'll talk about the reaction using 1-bromoethane as a typical halogenoalkane. You get a mixture of amines formed together with their salts. The reactions happen one after another.

The reaction happens in two stages. In the first stage, a salt is formed - in this case, ethylammonium bromide. This is just like ammonium bromide, except that one of the hydrogens in the ammonium ion is replaced by an ethyl group.

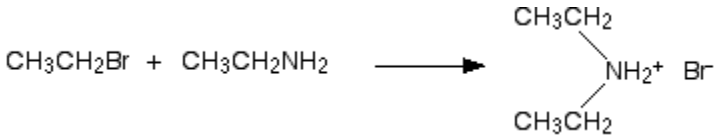
$$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_3^+Br^- \tag{26.7.4}$$

There is then the possibility of a reversible reaction between this salt and excess ammonia in the mixture.

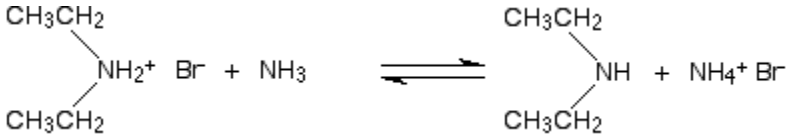
$$CH_3CH_2NH_3^+Br^- + NH_3 \rightleftharpoons CH_3CH_2NH_2 + NH_4^+Br^- \tag{26.7.5}$$

The ammonia removes a hydrogen ion from the ethylammonium ion to leave a primary amine - ethylamine. The more ammonia there is in the mixture, the more the forward reaction is favored.

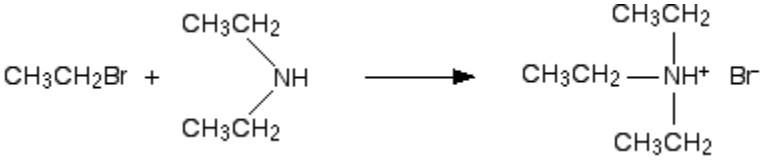
The reaction does not stop at a primary amine. The ethylamine also reacts with bromoethane - in the same two stages as before. In the first stage, you get a salt formed - this time, diethylammonium bromide. Think of this as ammonium bromide with two hydrogens replaced by ethyl groups.



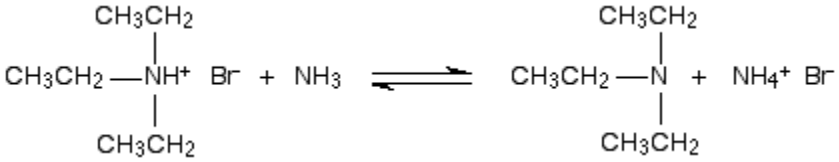
There is again the possibility of a reversible reaction between this salt and excess ammonia in the mixture.



The ammonia removes a hydrogen ion from the diethylammonium ion to leave a secondary amine - diethylamine. A secondary amine is one which has two alkyl groups attached to the nitrogen. The reaction does not stop! The diethylamine also reacts with bromoethane - in the same two stages as before. In the first stage, you get triethylammonium bromide.



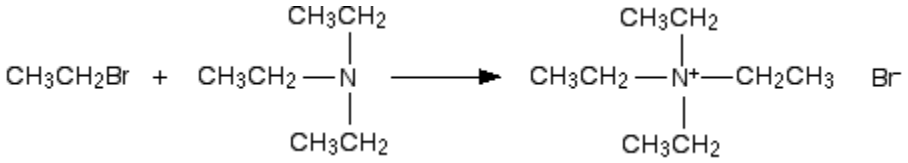
There is again the possibility of a reversible reaction between this salt and excess ammonia in the mixture.



The ammonia removes a hydrogen ion from the triethylammonium ion to leave a tertiary amine - triethylamine. A tertiary amine is one which has three alkyl groups attached to the nitrogen.

The final stage! The triethylamine reacts with bromoethane to give tetraethylammonium bromide - a quaternary ammonium salt (one in which

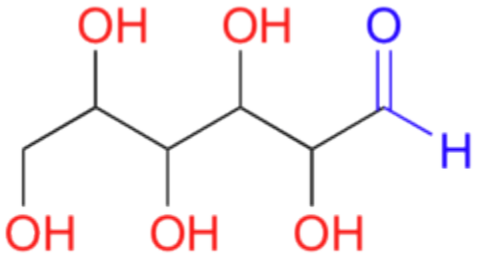
all four hydrogens have been replaced by alkyl groups).



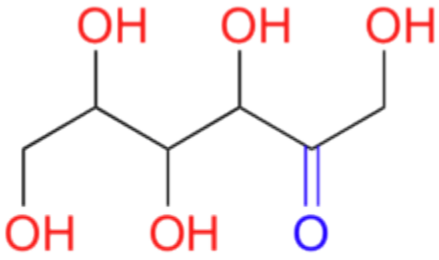
This time there isn't any hydrogen left on the nitrogen to be removed. The reaction stops here.

Molecules with Multiple Functional Groups

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**').

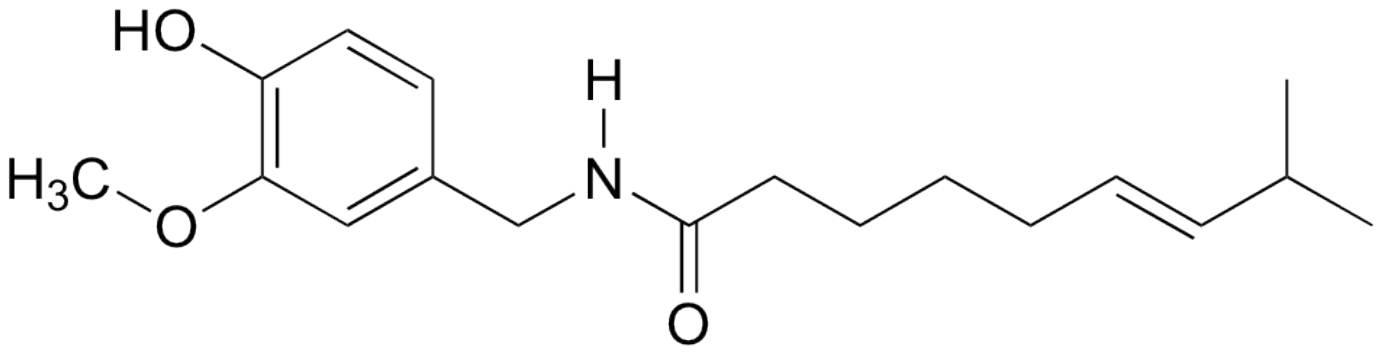


glucose



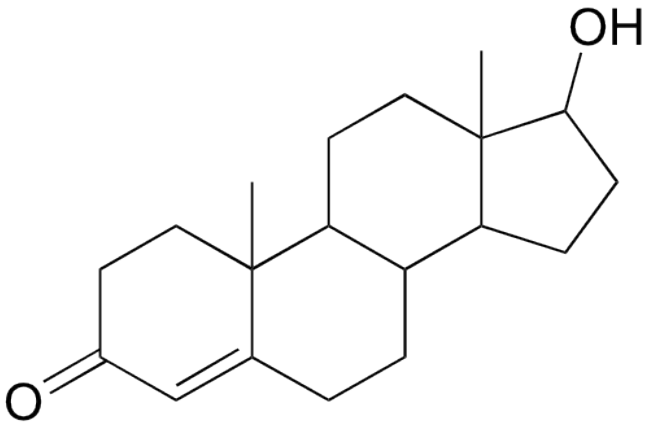
fructose

Capsaicin, the compound responsible for the heat in hot peppers, contains phenol, ether, amide, and alkene functional groups.

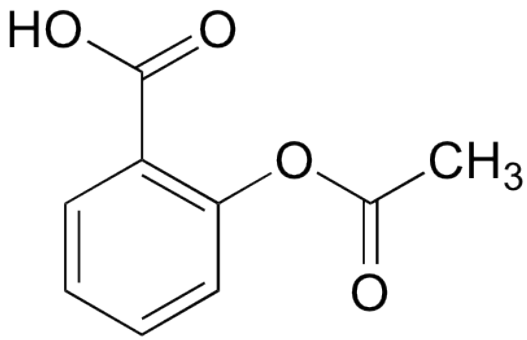


capsiacin

The male sex hormone testosterone contains ketone, alkene, and secondary alcohol groups, while acetylsalicylic acid (aspirin) contains aromatic, carboxylic acid, and ester groups.



testosterone



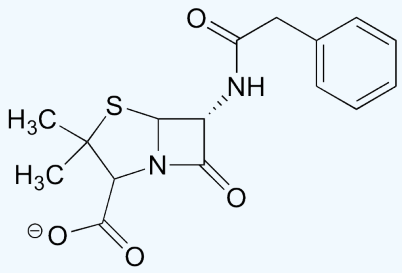
acetylsalicylic acid
(aspirin)

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.

Example 26.7.1

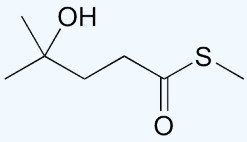
Identify the functional groups in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.

a)

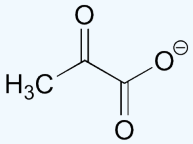


penicillin

b)

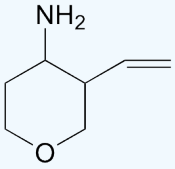


c)



pyruvate

d)



Example 26.7.2

Draw one example each (there are many possible correct answers) of compounds fitting the descriptions below, using line structures. Be sure to designate the location of all non-zero formal charges. All atoms should have complete octets (phosphorus may exceed the octet rule).

a. a compound with molecular formula $C_6H_{11}NO$ that includes alkene, secondary amine, and primary alcohol functional groups
b. an ion with molecular formula $C_3H_5O_6P^{2-}$ that includes aldehyde, secondary alcohol, and phosphate functional groups.
c. A compound with molecular formula C_6H_9NO that has an amide functional group, and does *not* have an alkene group.

Contributors and Attributions

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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26.8: From Molecular Formula to Molecular Structure

There are many ways one can go about determining the structure of an unknown organic molecule. Although, nuclear magnetic resonance (NMR) and infrared radiation (IR) are the primary ways of determining molecular structures, calculating the degrees of unsaturation is useful information since knowing the degrees of unsaturation make it easier for one to figure out the molecular structure; it helps one double-check the number of π bonds and/or cyclic rings.

Saturated vs. Unsaturated Molecules

In the lab, saturation may be thought of as the point when a solution cannot dissolve anymore of a substance added to it. In terms of degrees of unsaturation, a molecule only containing single bonds with no rings is considered saturated.

$CH_3CH_2CH_3$	chewiki_sat.bmp	chewiki_sat2 (3).bmp	1-methyoxypentane

Unlike saturated molecules, unsaturated molecules contain double bond(s), triple bond(s) and/or ring(s).

$CH_3CH{=}CHCH_3$	chewiki_unsat1.bmp	chewiki_unsat2.bmp	chewiki_unsat3.bmp	3-chloro-5-octyne

Calculating Degrees of Unsaturation (DoU)

Degree of Unsaturation (DoU) is also known as **Double Bond Equivalent**. If the molecular formula is given, plug in the numbers into this formula:

$$DoU = \frac{2C + 2 + N - X - H}{2} \tag{26.8.1}$$

- C is the number of carbons
- N is the number of nitrogens
- X is the number of halogens (F, Cl, Br, I)
- H is the number of hydrogens

As stated before, a saturated molecule contains only single bonds and no rings. Another way of interpreting this is that a saturated molecule has the maximum number of hydrogen atoms possible to be an acyclic alkane. Thus, the number of hydrogens can be represented by 2C+2, which is the general molecular representation of an alkane. As an example, for the molecular formula C_3H_4 the number of actual hydrogens needed for the compound to be saturated is 8 *[2C+2=(2x3)+2=8]*. The compound needs 4 more hydrogens in order to be fully saturated *(expected number of hydrogens-observed number of hydrogens=8-4=4)*. Degrees of unsaturation is equal to 2, or half the number of hydrogens the molecule needs to be classified as saturated. Hence, the DoB formula divides by 2. The formula subtracts the number of X's because a halogen (X) replaces a hydrogen in a compound. For instance, in chloroethane, C_2H_5Cl, there is one less hydrogen compared to ethane, C_2H_6.

For a compound to be saturated, there is one more hydrogen in a molecule when nitrogen is present. Therefore, we add the number of nitrogens (N). This can be seen with C_3H_9N compared to C_3H_8. Oxygen and sulfur are not included in the formula

because saturation is unaffected by these elements. As seen in alcohols, the same number of hydrogens in ethanol, C_2H_5OH, matches the number of hydrogens in ethane, C_2H_6.

The following chart illustrates the possible combinations of the number of double bond(s), triple bond(s), and/or ring(s) for a given degree of unsaturation. Each row corresponds to a different combination.

- One degree of unsaturation is equivalent to 1 ring or 1 double bond (1 π bond).
- Two degrees of unsaturation is equivalent to 2 double bonds, 1 ring and 1 double bond, 2 rings, or 1 triple bond (2 π bonds).

DoU	Possible combinations of rings/ bonds		
	# of rings	# of double bonds	# of triple bonds
1	1	0	0
	0	1	0
2	2	0	0
	0	2	0
	0	0	1
	1	1	0
3	3	0	0
	2	1	0
	1	2	0
	0	1	1
	0	3	0
	1	0	1

Remember, the degrees of unsaturation only gives the sum of double bonds, triple bonds and/or rings. For instance, a degree of unsaturation of 3 can contain 3 rings, 2 rings+1 double bond, 1 ring+2 double bonds, 1 ring+1 triple bond, 1 double bond+1 triple bond, *or* 3 double bonds.

Example: Benzene

What is the Degree of Unsaturation for Benzene?

Solution

The molecular formula for benzene is C_6H_6. Thus,

DoU= 4, where C=6, N=0,X=0, and H=6. 1 DoB can equal 1 ring or 1 double bond. This corresponds to benzene containing 1 ring and 3 double bonds.

chewiki_unsat1.bmp

However, when given the molecular formula C_6H_6, benzene is only one of many possible structures (isomers). The following structures all have DoB of 4 and have the same molecular formula as benzene.

4 DoB_2.bmp 4 DoB_3.bmp 4DoB_1.bmp

References

1. Vollhardt, K. P.C. & Shore, N. (2007). *Organic Chemistry* (5th Ed.). New York: W. H. Freeman. (473-474)

2. Shore, N. (2007). *Study Guide and Solutions Manual for Organic Chemistry* (5th Ed.). New York: W.H. Freeman. (201)

Problems

1. Are the following molecules saturated or unsaturated:
    1. chewiki_prob1a.bmp (b.)chewiki_prob2b.bmp (c.) chewiki_prob1c.bmp (d.) $C_{10}H_6N_4$
2. Using the molecules from 1., give the degrees of unsaturation for each.
3. Calculate the degrees of unsaturation for the following molecular formulas:
    1. (a.) C_9H_{20} (b.) C_7H_8 (c.) C_5H_7Cl (d.) $C_9H_9NO_4$
4. Using the molecular formulas from 3, are the molecules unsaturated or saturated.
5. Using the molecular formulas from 3, if the molecules are unsaturated, how many rings/double bonds/triple bonds are predicted?

Answers

1.

(a.) **unsaturated** (E*ven though rings only contain single bonds, rings are considered unsaturated.)*

(b.) **unsaturated**

(c.) **saturated**

(d.) **unsaturated**

2. *If the molecular structure is given, the easiest way to solve is to count the number of double bonds, triple bonds and/or rings. However, you can also determine the molecular formula and solve for the degrees of unsaturation by using the formula.*

(a.) **2**

(b.) **2** *(one double bond and the double bond from the carbonyl)*

(c.) **0**

(d.) **10**

3. *Use the formula to solve*

(a.) **0**

(b.) **4**

(c.) **2**

(d.) **6**

4.

(a.) **saturated**

(b.) **unsaturated**

(c.) **unsaturated**

(d.) **unsaturated**

5.

(a.) **0** (Remember-a saturated molecule only contains single bonds)

(b.) *The molecule can contain any of these combinations* **(i) 4 double bonds (ii) 4 rings (iii) 2 double bonds+2 rings (iv) 1 double bond+3 rings (v) 3 double bonds+1 ring (vi) 1 triple bond+2 rings (vii) 2 triple bonds (viii) 1 triple bond+1 double bond+1 ring (ix) 1 triple bond+2 double bonds**

(c.) (**i) 1 triple bond (ii) 1 ring+1 double bond (iii) 2 rings (iv) 2 double bonds**

(d.) **(i) 3 triple bonds (ii) 2 triple bonds+2 double bonds (iii) 2 triple bonds+1 double bond+1 ring (iv)...** *(As you can see, the degrees of unsaturation only gives the sum of double bonds, triple bonds and/or ring. Thus, the formula may give numerous possible structures for a given molecular formula.)*

Contributors

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27: REACTIONS OF ORGANIC COMPOUNDS

Petrucci: *General Chemistry*
Principles and Modern Applications

Template:HideTOC

- Topic hierarchy

27.1: Organic Reactions: An Introduction
27.2: Introduction to Substitution Reactions
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27.1: Organic Reactions: An Introduction

These are the four "prototypical" organic chemistry reactions, though several others which can be categorized as one of these are generally referred to by other names. Look at these reactions and ask yourself this question for each: **what bonds are broken, and what bonds are formed.**

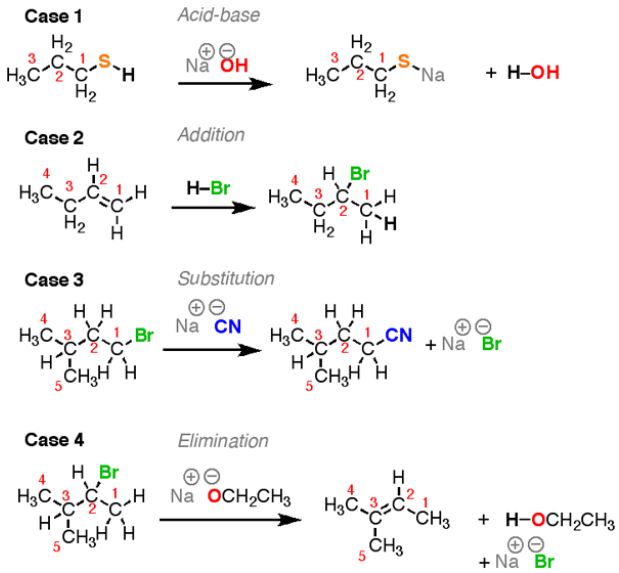


Figure 27.1.1: Four general reactions in Organic Chemistry. What bonds are broken, and what bonds are formed? A rearrangment reaction is not demonstrated.

At least 80% of the reactions students in organic chemistry fall into one of these four categories. The sooner you can get into the habit of recognizing bond formation and breakage the better off you will be. A fifth reaction is also discussed: rearrangement reactions.

Acid/Base Reactions

Another important category of organic reactions are straight-forward Brønsted–Lowry acid-base reactions (Figure 27.1.2.

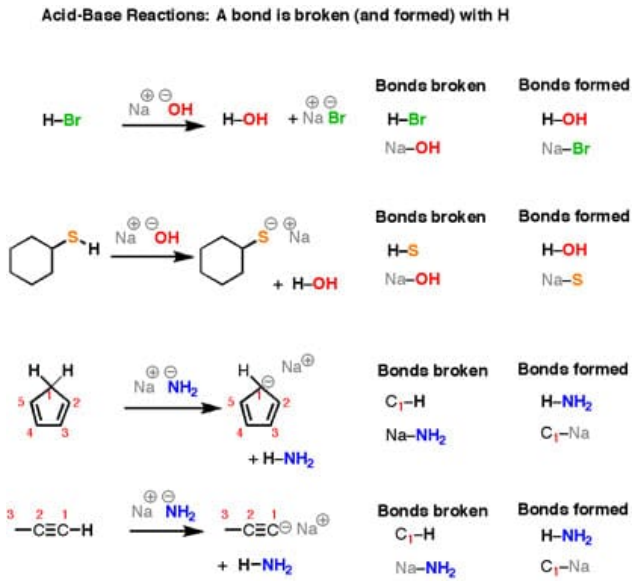
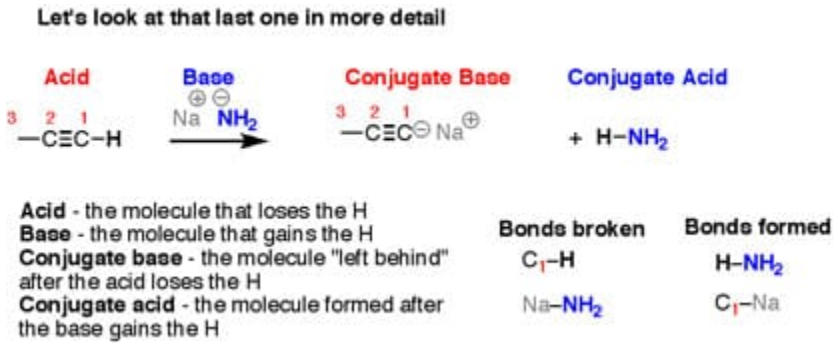


Figure 27.1.2: Acid/Base reactions

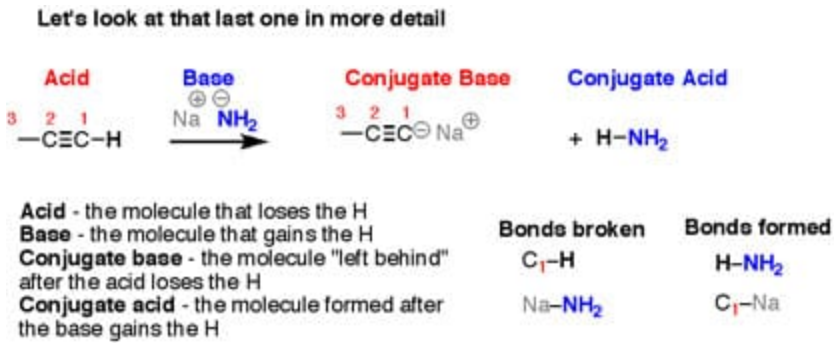
You'll notice that they might look very different on the surface – all those different structures! – **but the basic plot of each reaction is the same**. we are breaking an H-(atom) bond and forming an H-(atom) bond. At the same time we are also connecting the two "leftover" partners to form a **salt**, composed of two oppositely-charged ions. Let's look at that last reaction in more detail. Here, we are breaking a C-H bond and an (ionic) Na-NH2 bond, and forming an N-H bond as well as an (ionic) C-Na bond.



There are four "actors" in this reaction – as there are in **every** acid-base reaction – and we have names for all of them.

- The reactant where the bond to H is breaking is the **acid**.
- The reactant where the bond to H is forming is the **base**
- The product formed when the bond to H is **broken** is called the **conjugate base**.
- The product formed when the bond to H is **formed** is called the **conjugate acid.**

We can also draw the reverse of the previous reaction. Look at this carefully. we are still breaking a bond to H and forming a bond to H, but we've swapped everything. we are breaking N-H and C-Na, and forming N-Na and C-H. **It's still an acid-base reaction.**



However, **experiment** tells us that this reaction does not happen to any appreciable extent.

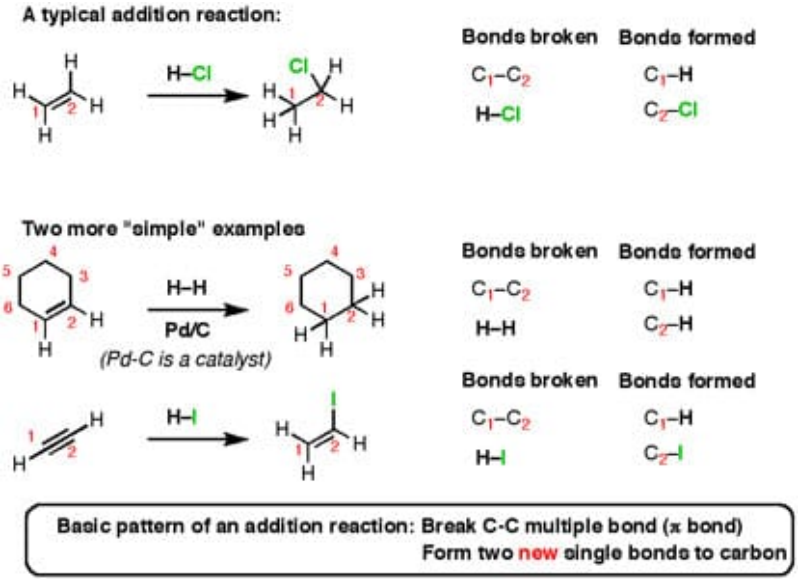
Exercise 27.1.1

In this acid/base reaction, which bonds are broken and with are formed, if any?

$$(CH_3{-}CH_2)_3N + HCl \rightarrow (CH_3{-}CH_2)_3NH^+ + Cl^-$$

Addition Reactions

When you take an alkene (or alkyne) and add certain types of reagents to them, you get results like this. See if you can recognize the bonds formed and broken.



Here's the basic pattern: break a C-C multiple bond (also called a π bond) and form two new single bonds ("σ-bonds" to carbon). This reaction is called an "addition reaction" and it's an extremely common type of reaction. Note that the reaction occurs **only** at the carbons that are a part of a multiple bond – nothing else on the molecule is affected.

Exercise 27.1.2

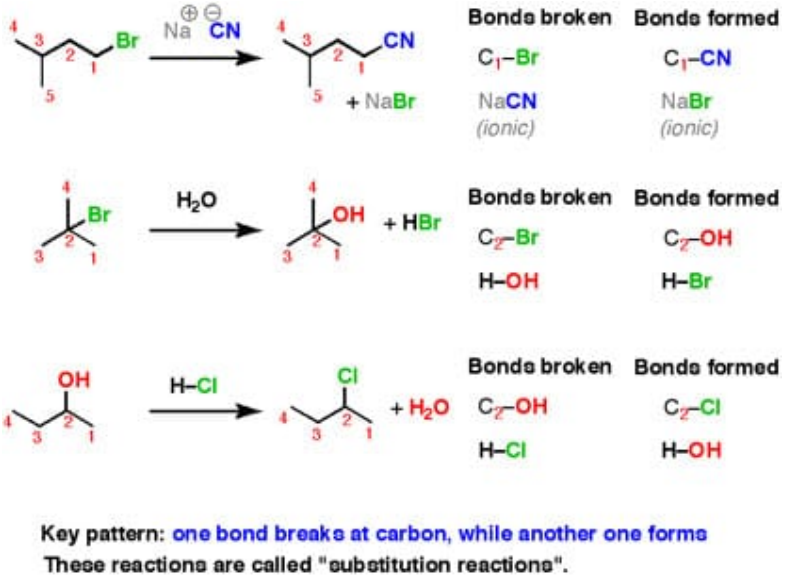
In this addition reaction, which bonds are broken and with are formed, if any?

$$CH_3{-}C(=O){-}CH_3 \xrightarrow[H^+/H_2O]{LiAlH_4} CH_3{-}CH(OH){-}CH_3$$

Note: This reaction could be described as a (nucleophilic) addition reaction or a reduction.

Substitution Reaction

Here are three examples of nucleophilic substitution reactions.



In each case, we are **breaking a bond at carbon, and forming a new bond at carbon.** This is an extremely common pattern for organic chemistry reactions. Here's some interesting results that **experiments** tell us. We don't get this information by thinking about what happens and predicting – we have to *interrogate* nature in order to get her to give up her secrets.

Exercise 27.1.3

In this substitution reaction , which bonds are broken and with are formed, if any?

$$\mathrm{CH_3{-}C(=O){-}OH + CH_3{-}OH \xrightarrow[\Delta \text{ and reflux}]{H_2SO_4} CH_3{-}C(=O){-}O{-}CH_3 + H_2O}$$

Note: This reaction would usually be called a condensation reaction.

Elimination Reactions

Let's look at two simple cases. One important thing to keep in mind: although you see "Na OCH3" written here, the "Na+" (sodium) is not important for our purposes. It could alternatively be K+ (potassium) or Li+ (lithium). It's just balancing the negative charge on the oxygen. When you take an alkyl halide and add a strong base (such as $\mathrm{NaOCH_3}$ or $\mathrm{NaOCH_2CH_3}$) a reaction occurs. See if you can recognize the bonds broken and formed.

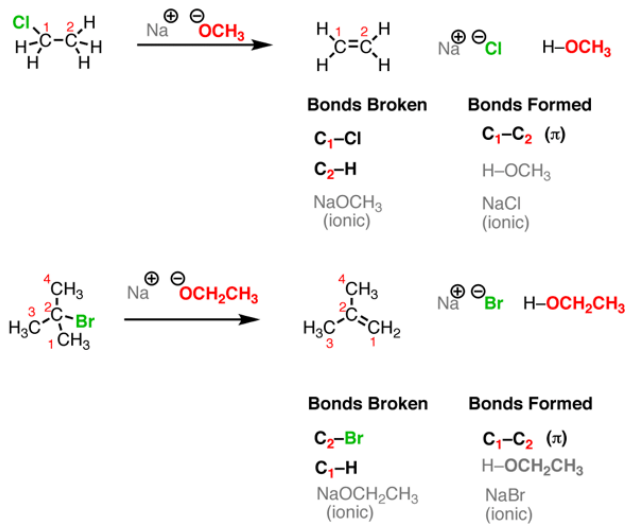


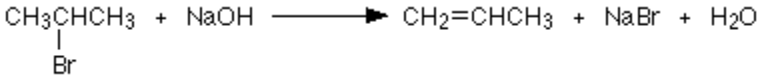
Figure 27.1.3: Elimination Reactions.These are the reverse of addiion reactions.

This reaction results in the **forming** of a new C-C double bond (π bond) and breaking two single bonds to carbon (in these cases, one of them is H and the other is a halide such as Cl or Br). We are also forming a new bond between H and the O. So in this respect, this reaction incorporates a pattern we have seen before – an acid-base reaction. Finally, we also form a salt in this reaction. Since we are primarily interested in the organic product (that is, the one containing carbon), you might find that the salt byproduct is not written in some reaction schemes, but that doesn't mean that it's not there.

Note

The three events in the elimination reactyio of Figure 27.1.3 (formation of C-C π bond, breakage of two adjacent carbon sigma bonds) are the exact **opposite** of the addition reactions discussed above.

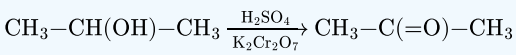
Another example of an elimination is when 2-bromopropane is heated under reflux with a concentrated solution of sodium or potassium hydroxide in ethanol. Heating under reflux involves heating with a condenser placed vertically in the flask to avoid loss of volatile liquids. Propene is formed and, because this is a gas, it passes through the condenser and can be collected.



Everything else present (including anything formed in the alternative substitution reaction) will be trapped in the flask.

Exercise 27.1.4

In this elimination reaction, which bonds are broken and with are formed, if any?

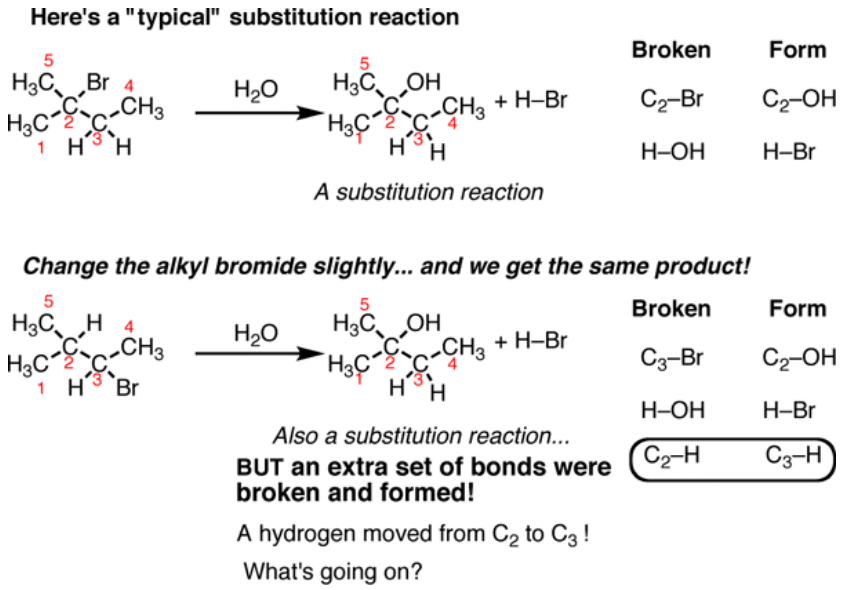


Note: This reaction could also be described an oxidation reaction.

Rearrangement Reactions

Rearrangement reactions can accompany many of the reactions we've previously covered such as substitution, addition, and elimination reactions. These reactions are comparatively rare. In fact, if you don't look closely, sometimes you can miss the fact

that a rearrangement reaction has occurred. Let's look at a substitution reaction first.



On the top is a "typical" substitution reaction: we are taking an alkyl halide and adding water. The C-Br bond is broken and a C-OH bond is formed. If you look at the table on the right you'll see this follows the typical pattern of substitution reactions. However if we change **one** thing about this alkyl halide – move the bromine to C-3 instead of C-2 – now when we run this reaction we see a different product emerge. It is also a substitution reaction (we are replacing Br with OH) but it's on a **different carbon.** That's because if you look closely, you can see there are actually 3 bonds broken and 3 bonds formed. The C2-H bond broke and the C3-H bond formed.

Exercise 27.1.5

In this Rearrangement reaction, which bonds are broken and with are formed, if any?

$$\mathrm{CH_3{-}CH_2{-}CH_2{-}C(OH){=}CH_2 \rightarrow CH_3{-}CH_2{-}CH_2{-}C(=O){-}CH_3}$$

Note: This reaction could also be described an oxidation reaction.

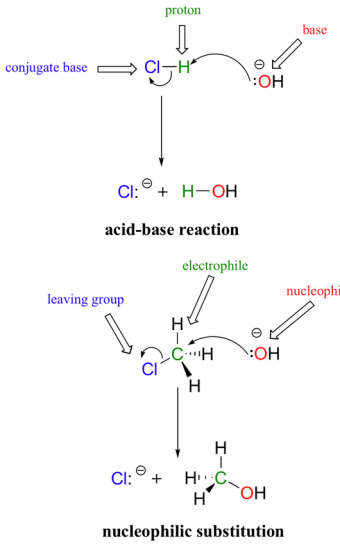
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27.2: Introduction to Substitution Reactions

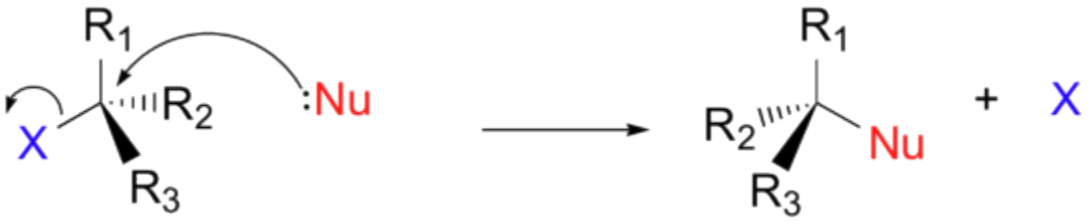
In many ways, the proton transfer process in a Brønsted-Lowry acid-base reaction can be thought of as simply a special kind of nucleophilic substitution reaction, one in which the electrophile is a hydrogen rather than a carbon.



In both reaction types, we are looking at very similar players: an electron-rich species (the nucleophile/base) attacks an electron-poor species (the electrophile/proton), driving off the leaving group/conjugate base.In the next few sections, we are going to be discussing some general aspects of nucleophilic substitution reactions, and in doing so it will simplify things greatly if we can use some abbreviations and generalizations before we dive into real examples.

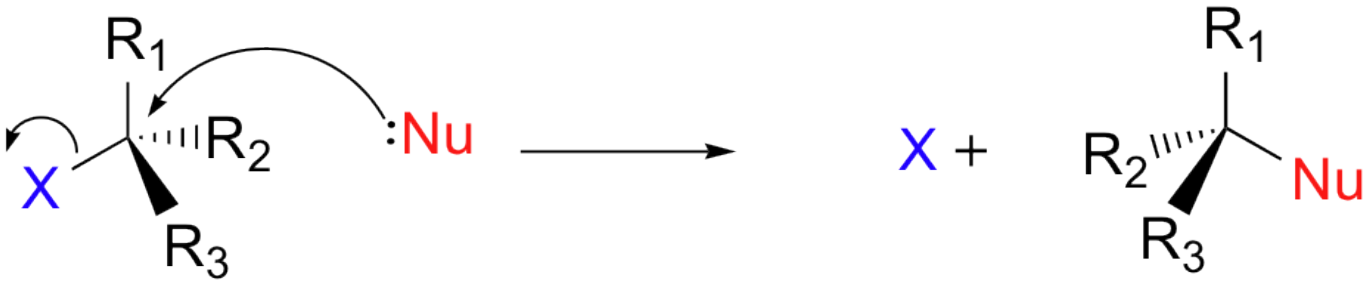
Instead of showing a specific nucleophile like hydroxide, we will simply refer to the nucleophilic reactant as 'Nu'. In a similar fashion, we will call the leaving group 'X'. We will see as we study actual reactions that leaving groups are sometimes negatively charged, sometimes neutral, and sometimes positively charged. We will also see some examples of nucleophiles that are negatively charged and some that are neutral. Therefore, in this general picture we will not include a charge designation on the 'X' or 'Nu' species. In the same way, we will see later that nucleophiles and leaving groups are sometimes protonated and sometimes not, so for now, for the sake of simplicity, we will not include protons on 'Nu' or 'X'. We will generalize the three other groups bonded on the electrophilic central carbon as R_1, R_2, and R_3: these symbols could represent hydrogens as well as alkyl groups. Finally, in order to keep figures from becoming too crowded, we will use in most cases the line structure convention in which the central, electrophilic carbon is not drawn out as a 'C'.

Here, then, is the generalized picture of a concerted (single-step) nucleophilic substitution reaction:

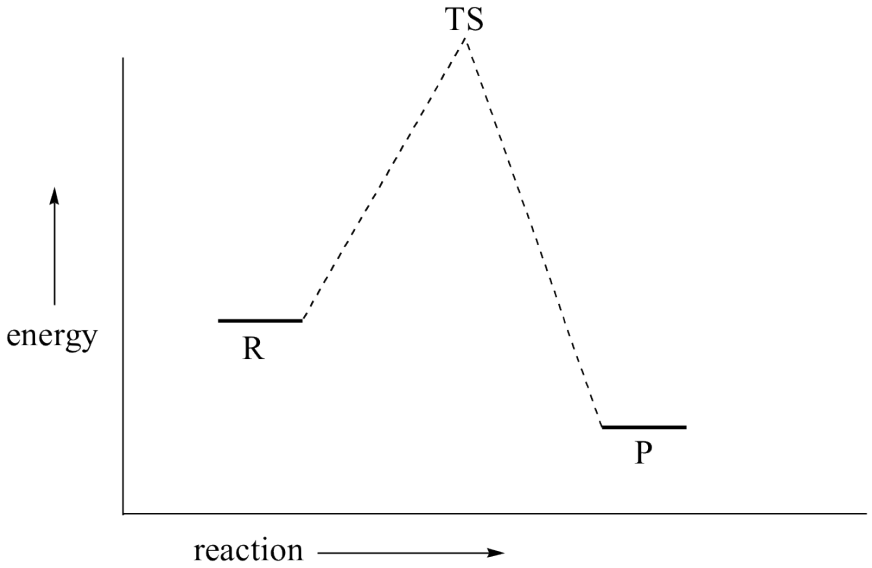


Associative nucleophilic substitution: the S_N2 reaction

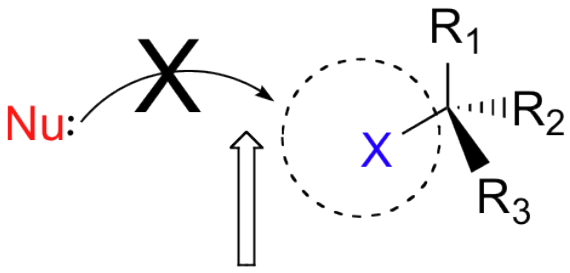
There are two mechanistic models for how a nucleophilic substitution reaction can proceed. In the first picture, the reaction takes place in a single step, and bond-forming and bond-breaking occur simultaneously.



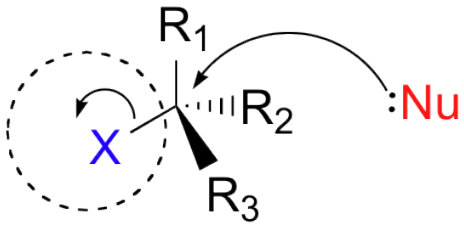
This is called an '**associative**', or '**S_N2**' mechanism. In the term S_N2, S stands for 'substitution', the subscript N stands for 'nucleophilic', and the number 2 refers to the fact that this is a **bimolecular reaction**: the overall rate depends on a step in which two separate molecules (the nucleophile and the electrophile) collide. A potential energy diagram for this reaction shows the transition state (TS) as the highest point on the pathway from reactants to products.



If you look carefully at the progress of the S_N2 reaction, you will realize something very important about the outcome. The nucleophile, being an electron-rich species, must attack the electrophilic carbon from the *back side* relative to the location of the leaving group. Approach from the front side simply doesn't work: the leaving group - which is also an electron-rich group - blocks the way.

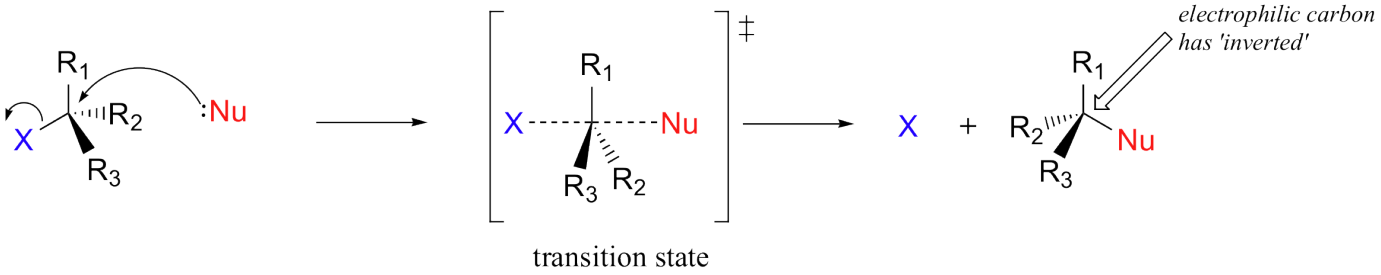


nucleophilic attack is blocked from the front side . . .



. . .so attack occurs from the back side

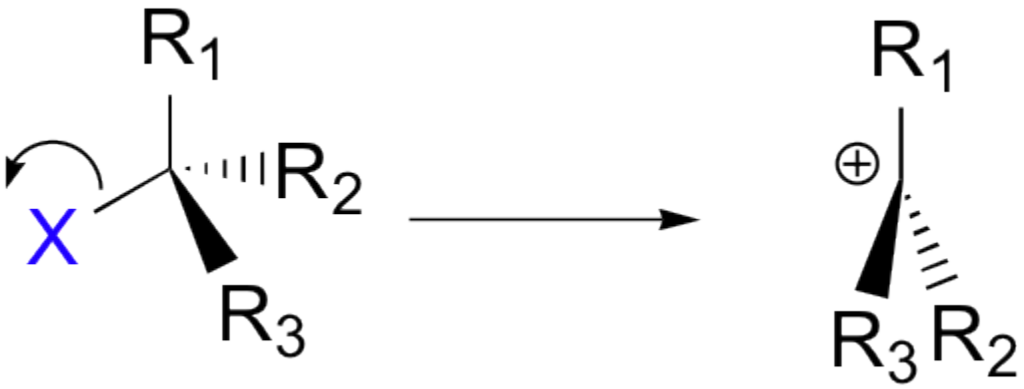
The result of this backside attack is that the stereochemical configuration at the central carbon *inverts* as the reaction proceeds. In a sense, the molecule is turned inside out. At the transition state, the electrophilic carbon and the three 'R' substituents all lie on the same plane.



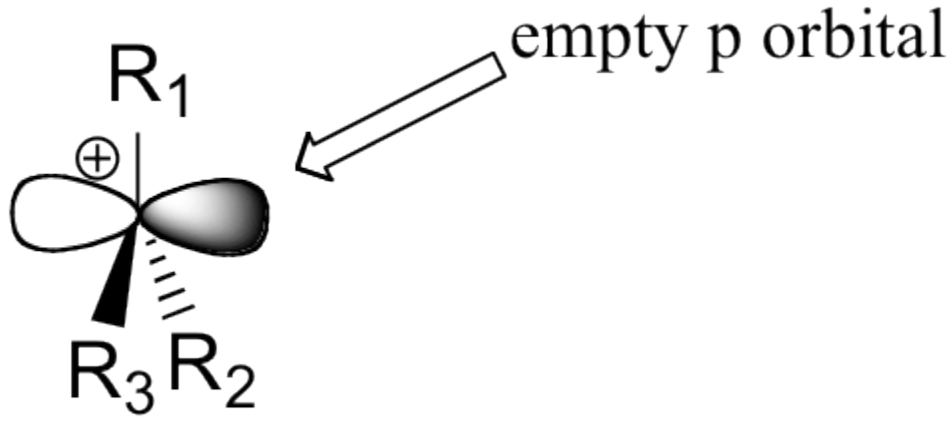
What this means is that S_N2 reactions whether enzyme catalyzed or not, are inherently stereoselective: when the substitution takes place at a stereocenter, we can confidently predict the stereochemical configuration of the product.

Dissociative nucleophilic substitution: the S_N1 reaction

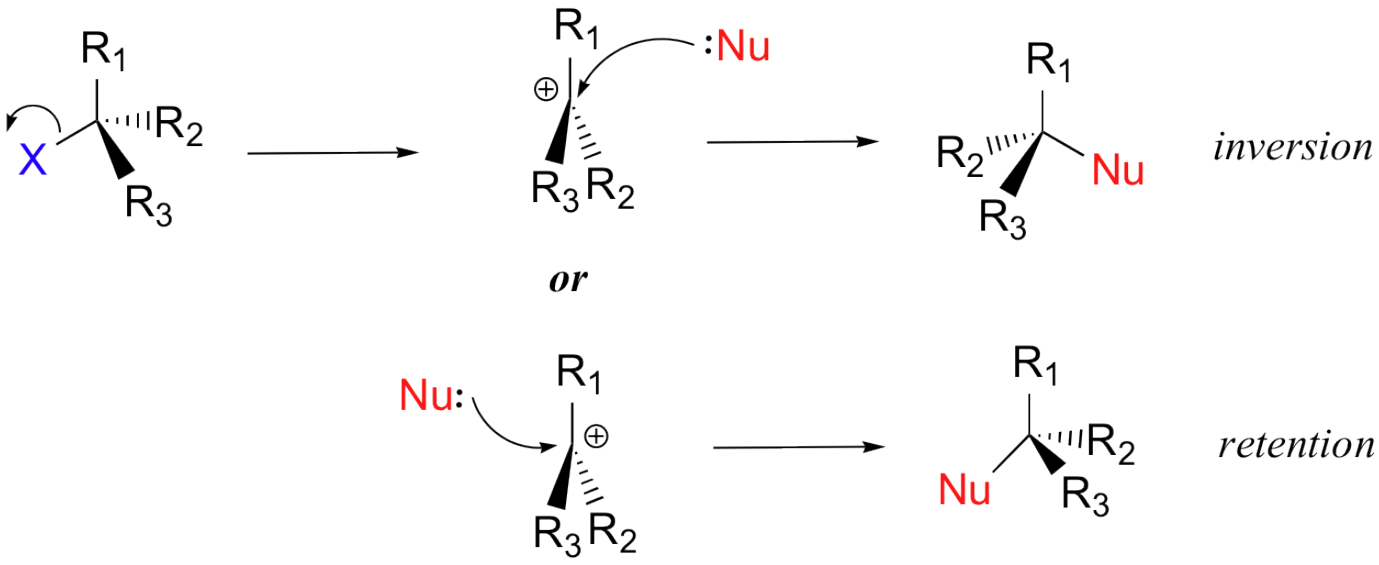
A second model for a nucleophilic substitution reaction is called the '**dissociative**', or '**S_N1**' mechanism: in this picture, the C-X bond breaks *first*, before the nucleophile approaches:



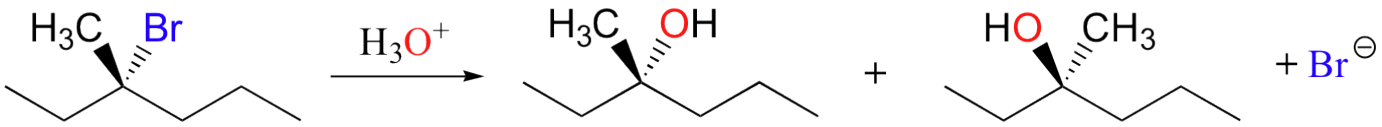
This results in the formation of a carbocation: because the central carbon has only three bonds, it bears a formal charge of +1. Recall that a carbocation should be pictured as sp^2 hybridized, with trigonal planar geometry. Perpendicular to the plane formed by the three sp^2 hybrid orbitals is an empty, unhybridized *p* orbital.



In the second step of this two-step reaction, the nucleophile attacks the empty, 'electron hungry' *p* orbital of the carbocation to form a new bond and return the carbon to tetrahedral geometry.

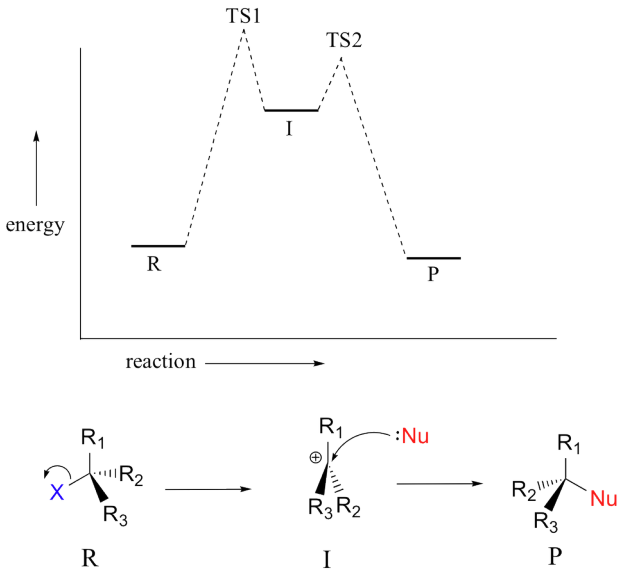


We saw that S_N2 reactions result specifically in inversion of stereochemistry at the electrophilic carbon center. What about the stereochemical outcome of S_N1 reactions? In the model S_N1 reaction shown above, the leaving group dissociates completely from the vicinity of the reaction before the nucleophile begins its attack. Because the leaving group is no longer in the picture, the nucleophile is free to attack from either side of the planar, sp^2-hybriduzed carbocation electrophile. This means that about half the time the product has the same stereochemical configuration as the starting material (retention of configuration), and about half the time the stereochemistry has been inverted. In other words, *racemization* has occurred at the carbon center. As an example, the tertiary alkyl bromide below would be expected to form a racemic mix of *R* and *S* alcohols after an S_N1 reaction with water as the incoming nucleophile.



While most nonenzymatic S_N1 reactions are not stereoselective, we will see later that enzyme-catalyzed nucleophilic substitution reactions - whether S_N1 or S_N2 - almost always *are* stereoselective. The direct result of an enzymatic nucleophilic substitution reaction is more often than not *inversion* of configuration - this is because the leaving group usually remains bound in the enzyme's active site long enough to block a nucleophilic attack from that side. This does not mean, however, that enzymes can only catalyze substitution reactions with inversion of configuration: we will see in the next chapter (section 9.2) an example of an enzymatic nucleophilic substitution reaction in which the overall result is 100% *retention* of configuration.

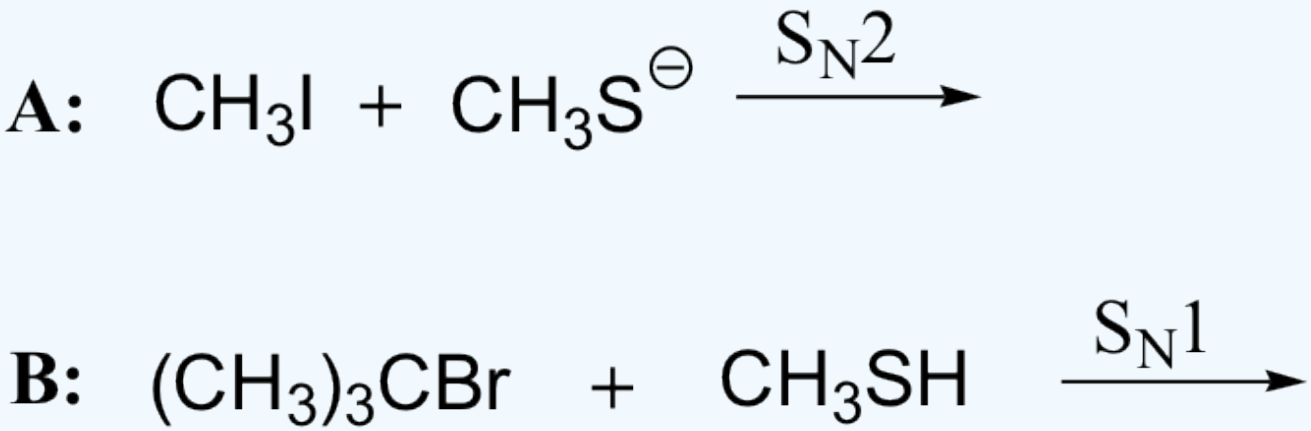
In the S_N1 reaction we see an example of a reaction intermediate, a very important concept in the study of organic reaction mechanisms that was first introduced in Chapter 6. Recall that many important organic reactions do not occur in a single step; rather, they are the sum of two or more discreet bond-forming / bond-breaking steps, and involve transient intermediate species that go on to react very quickly. In the S_N1 reaction, the carbocation species is a reaction intermediate. A potential energy diagram for an S_N1 reaction shows that the carbocation intermediate can be visualized as a kind of valley in the path of the reaction, higher in energy than both the reactant and product but lower in energy than the two transition states.



Recall (section 6.2) that the first step of the reaction above, in which two charged species are formed from a neutral molecule, is much the slower of the two steps, and is therefore rate-determining. This is illustrated by the energy diagram, where the activation energy for the first step is higher than that for the second step. Also recall that an S_N1 reaction has *first order* kinetics, because the rate determining step involves one molecule splitting apart, not two molecules colliding.

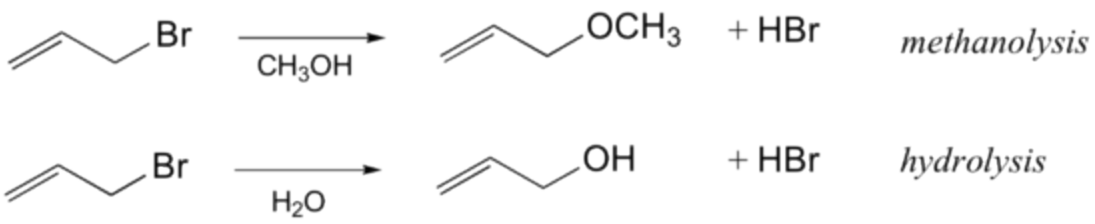
Example

Consider two nucleophilic substitutions that occur uncatalyzed in solution. Assume that reaction A is S_N2, and reaction B is S_N1. Predict, in each case, what would happen to the rate of the reaction if the concentration of the nucleophile were doubled, while all other conditions remained constant.



Solution (8.5)

Many S_N1 reactions are of a class that are referred to as **solvolysis**, where a solvent molecule participates in the reaction as a nucleophile. The S_N1 reaction of allyl bromide in methanol is an example of what we would call **methanolysis**, while if water is the solvent the reaction would be called **hydrolysis**:



Because water and alcohols are relatively weak nucleophiles, they are unlikely to react in an S_N2 fashion.

Nucleophilic substitutions occur at sp^3-hybridized carbons

One more important point must be made before continuing: nucleophilic substitutions as a rule occur at sp^3-hybridized carbons, and *not* where the leaving group is attached to an sp^2-hybridized carbon::



Bonds on sp^2-hybridized carbons are inherently shorter and stronger than bonds on sp^3-hybridized carbons (section 1.5C), meaning that it is harder to break the C-X bond in these substrates. S_N2 reactions of this type are unlikely also because the (hypothetical) electrophilic carbon is protected from nucleophilic attack by electron density in the p bond. S_N1 reactions are highly unlikely, because the resulting carbocation intermediate, which would be sp-hybridized, would be very unstable (we'll discuss the relative stability of carbocation intermediates in section 8.4B).

Before we look at some real-life nucleophilic substitution reactions in the next chapter, we will spend some time in the remainder of this chapter focusing more closely on the three principal partners in the nucleophilic substitution reaction: the nucleophile, the electrophile, and the leaving group.

What makes a nucleophile?

As a general rule, nucleophile substitution reactions that involve powerful nucleophiles tend to occur with S_N2 mechanisms, while reactions with weaker nucleophiles tend to be S_N1. But what makes a group a strong or weak nucleophile? Nucleophilic functional groups are those which have electron-rich atoms able to donate a pair of electrons to form a new covalent bond. In both laboratory and biological organic chemistry, the most relevant nucleophilic atoms are oxygen, nitrogen, and sulfur, and the most common nucleophilic functional groups are water, alcohols, phenols, amines, thiols, and occasionally carboxylates.

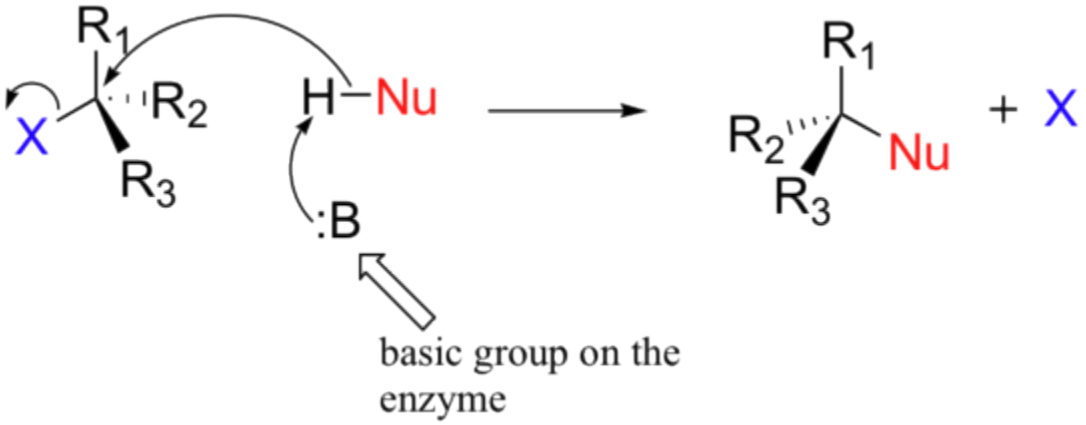
Of course, carbons can also be nucleophiles - otherwise how could new carbon-carbon bonds be formed in the synthesis of large organic molecules like DNA or fatty acids? When thinking about nucleophiles, the first thing to recognize is that, for the most part, the same quality of 'electron-richness' that makes a something nucleophilic also makes it basic: *nucleophiles can be bases, and*

bases can be nucleophiles. It should not be surprising, then, that most of the trends in basicity that we have already discussed also apply to nucleophilicity.

Protonation states and nucleophilicity

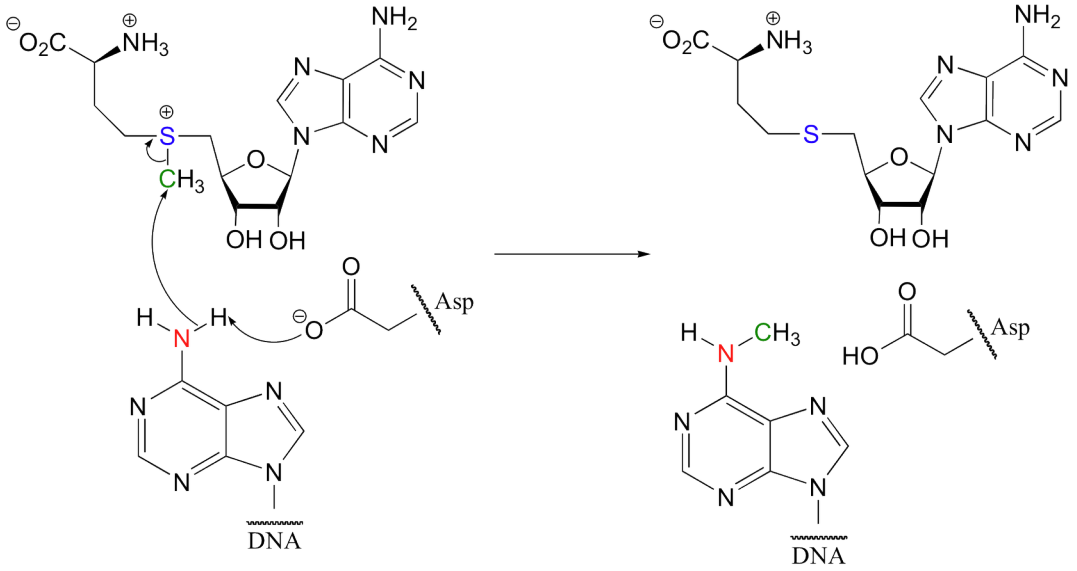
The protonation state of a nucleophilic atom has a very large effect on its nucleophilicity. This is an idea that makes intuitive sense: a hydroxide ion is much more nucleophilic (and basic) than a water molecule, because the negatively charged oxygen on the hydroxide ion carries greater electron density than the oxygen atom of a neutral water molecule. In practical terms, this means that a hydroxide nucleophile will react in an S_N2 reaction with methyl bromide much faster (about 10,000 times faster) than a water nucleophile.

A neutral amine is nucleophilic, whereas a protonated ammonium cation is not. This is why enzymes which have evolved to catalyze nucleophilic reactions often have a basic amino acid side chain poised in position to accept a proton from the nucleophilic atom as the nucleophilic attack occurs.



Depending on the specific reaction being discussed, deprotonation of the nucleophile might occur before, during, or after the actual nucleophilic attack. In general for enzymatic reactions, however, it is most accurate to depict the proton abstraction and nucleophilic attack occurring simultaneously.

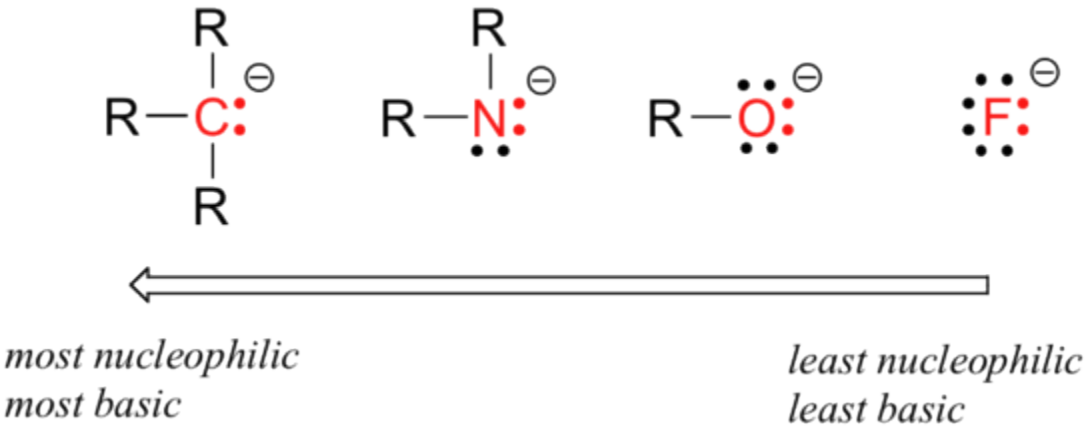
The basic enzymatic group could be a histidine, a neutral (deprotonated) arginine or lysine, or a negatively-charged (deprotonated) aspartate, glutamate, or tyrosine. For example, a more complete picture of the DNA methylation reaction we saw in section 8.1 shows an aspartate from the enzyme's active site accepting a proton from the nucleophilic amine as it attacks the carbon electrophile.



As it is deprotonated by the aspartate, the amine nitrogen becomes more electron-rich, and therefore more nucleophilic.

Periodic trends and solvent effects in nucleophilicity

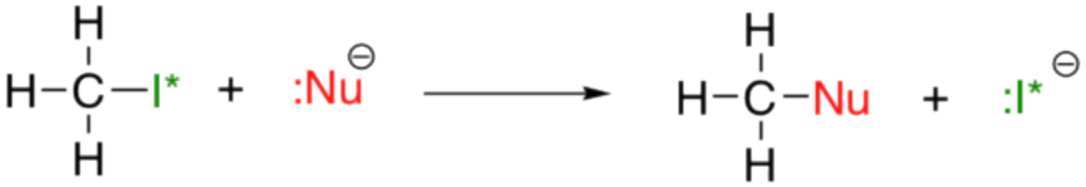
There are predictable periodic trends in nucleophilicity. Moving horizontally across the second row of the table, the trend in nucleophilicity parallels the trend in basicity:



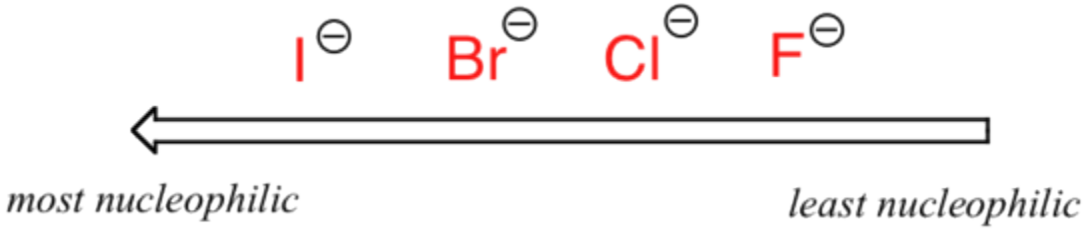
The reasoning behind the horizontal nucleophilicity trend is the same as the reasoning behind the basicity trend: more electronegative elements hold their electrons more tightly, and are less able to donate them to form a new bond. This horizontal trends also tells us that amines are more nucleophilic than alcohols, although both groups commonly act as nucleophiles in both laboratory and biochemical reactions.

Recall from section 7.3A that the basicity of atoms decreases as we move vertically down a column on the periodic table: thiolate ions are less basic than alkoxide ions, for example, and bromide ion is less basic than chloride ion, which in turn is less basic than fluoride ion. Recall also that this trend can be explained by considering the increasing size of the 'electron cloud' around the larger ions: the electron density inherent in the negative charge is spread around a larger area, which tends to increase stability (and thus reduce basicity).

The vertical periodic trend for nucleophilicity is somewhat more complicated that that for basicity: depending on the solvent that the reaction is taking place in, the nucleophilicity trend can go in either direction. Let's take the simple example of the S_N2 reaction below:



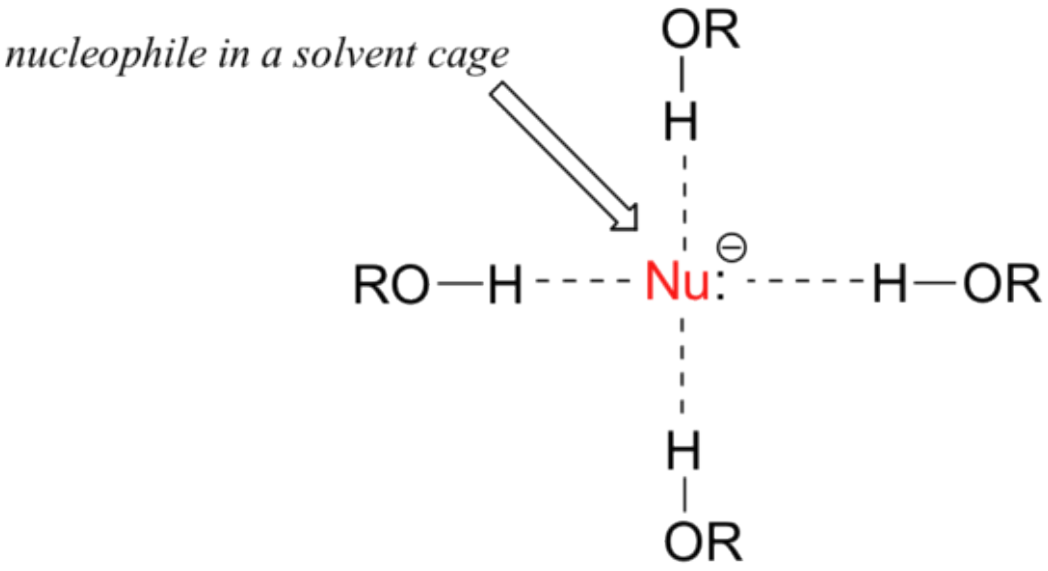
. . .where Nu^- is one of the halide ions: fluoride, chloride, bromide, or iodide, and the leaving group I* is a radioactive isotope of iodine (which allows us to distinguish the leaving group from the nucleophile in that case where both are iodide). If this reaction is occurring in a **protic solvent** (that is, a solvent that has a hydrogen bonded to an oxygen or nitrogen - water, methanol and ethanol are the most important examples), then the reaction will go fastest when iodide is the nucleophile, and slowest when fluoride is the nucleophile, reflecting the relative strength of the nucleophile.



Relative nucleophilicity in a protic solvent

This of course, is opposite that of the vertical periodic trend for basicity, where iodide is the *least* basic (you may want to review the reasoning for this trend in section 7.3A). What is going on here? Shouldn't the stronger base, with its more reactive unbonded valence electrons, also be the stronger nucleophile?

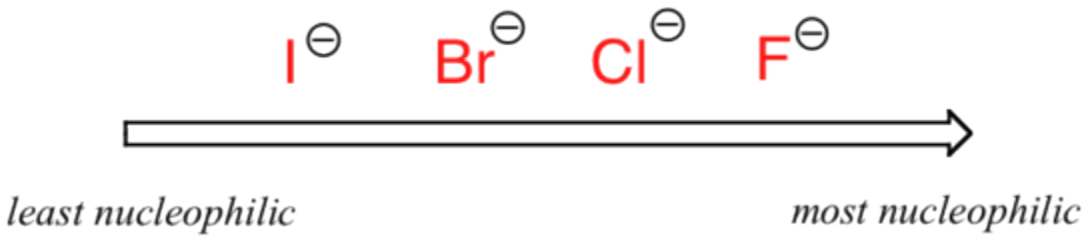
As mentioned above, it all has to do with the solvent. Remember, we are talking now about the reaction running in a *protic* solvent like ethanol. Protic solvent molecules form very strong ion-dipole interactions with the negatively-charged nucleophile, essentially creating a 'solvent cage' around the nucleophile:



In order for the nucleophile to attack the electrophile, it must break free, at least in part, from its solvent cage. The lone pair electrons on the larger, less basic iodide ion interact less tightly with the protons on the protic solvent molecules - thus the iodide nucleophile is better able to break free from its solvent cage compared the smaller, more basic fluoride ion, whose lone pair electrons are bound more tightly to the protons of the cage.

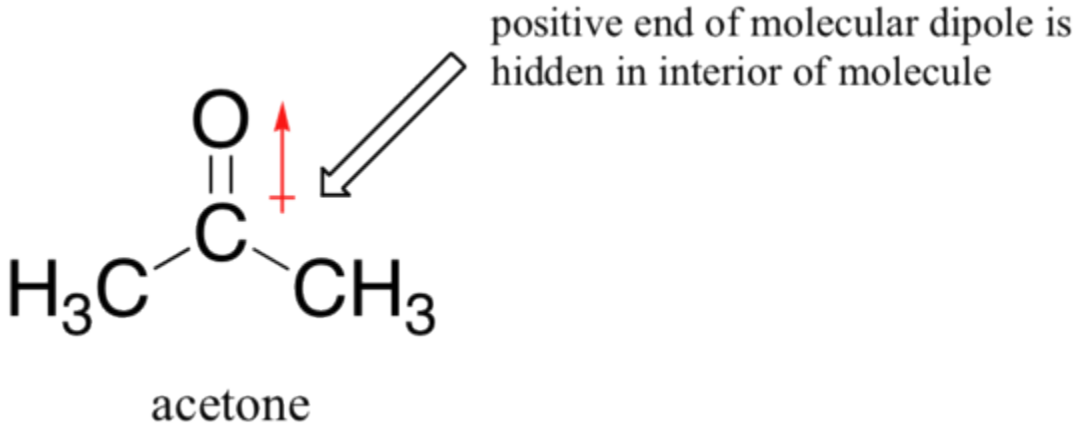
The picture changes if we switch to a **polar aprotic solvent**, such as acetone, in which there is a molecular dipole but *no*

hydrogens bound to oxygen or nitrogen. Now, fluoride is the best nucleophile, and iodide the weakest.



Relative nucleophilicity in a polar aprotic solvent

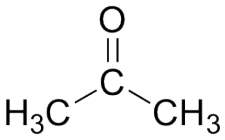
The reason for the reversal is that, with an aprotic solvent, the ion-dipole interactions between solvent and nucleophile are much weaker: the positive end of the solvent's dipole is hidden in the interior of the molecule, and thus it is shielded from the negative charge of the nucleophile.



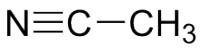
acetone

A weaker solvent-nucleophile interaction means a weaker solvent cage for the nucleophile to break through, so the solvent effect is much less important, and the more basic fluoride ion is also the better nucleophile.

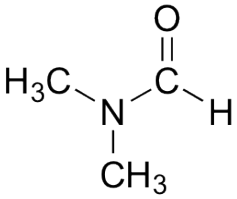
Why not use a completely nonpolar solvent, such as hexane, for this reaction, so that the solvent cage is eliminated completely? The answer to this is simple - the nucleophile needs to be in solution in order to react at an appreciable rate with the electrophile, and a solvent such as hexane will not solvate an a charged (or highly polar) nucleophile at all. That is why chemists use polar aprotic solvents for nucleophilic substitution reactions in the laboratory: they are polar enough to solvate the nucleophile, but not so polar as to lock it away in an impenetrable solvent cage. In addition to acetone, three other commonly used polar aprotic solvents are acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).



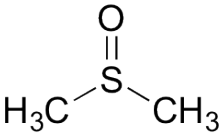
acetone



acetonitrile



dimethylformamide (DMF)

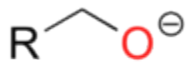


dimethylsulfoxide (DMSO)

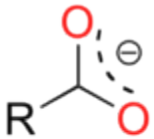
In biological chemistry, where the solvent is protic (water), the most important implication of the periodic trends in nucleophilicity is that thiols are more powerful nucleophiles than alcohols. The thiol group in a cysteine amino acid, for example, is a powerful nucleophile and often acts as a nucleophile in enzymatic reactions, and of course negatively-charged thiolates (RS^-) are even more nucleophilic. This is not to say that the hydroxyl groups on serine, threonine, and tyrosine do not also act as nucleophiles - they do.

Resonance effects on nucleophilicity

Resonance effects also come into play when comparing the inherent nucleophilicity of different molecules. The reasoning involved is the same as that which we used to understand resonance effects on basicity (see section 7.3C). If the electron lone pair on a heteroatom is delocalized by resonance, it is inherently less reactive - meaning less nucleophilic, and also less basic. An alkoxide ion, for example, is more nucleophilic and more basic than a carboxylate group, even though in both cases the nucleophilic atom is a negatively charged oxygen. In the alkoxide, the negative charge is localized on a single oxygen, while in the carboxylate the charge is delocalized over two oxygen atoms by resonance.

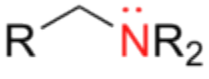


alkoxide ion:
charge is localized
more nucleophilic

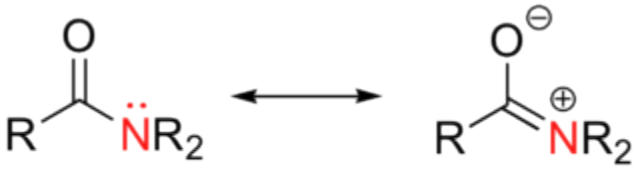


carboxylate ion:
charge is spread over both oxygens
less nucleophilic

The nitrogen atom on an amide is less nucleophilic than the nitrogen of an amine, due to the resonance stabilization of the nitrogen lone pair provided by the amide carbonyl group.



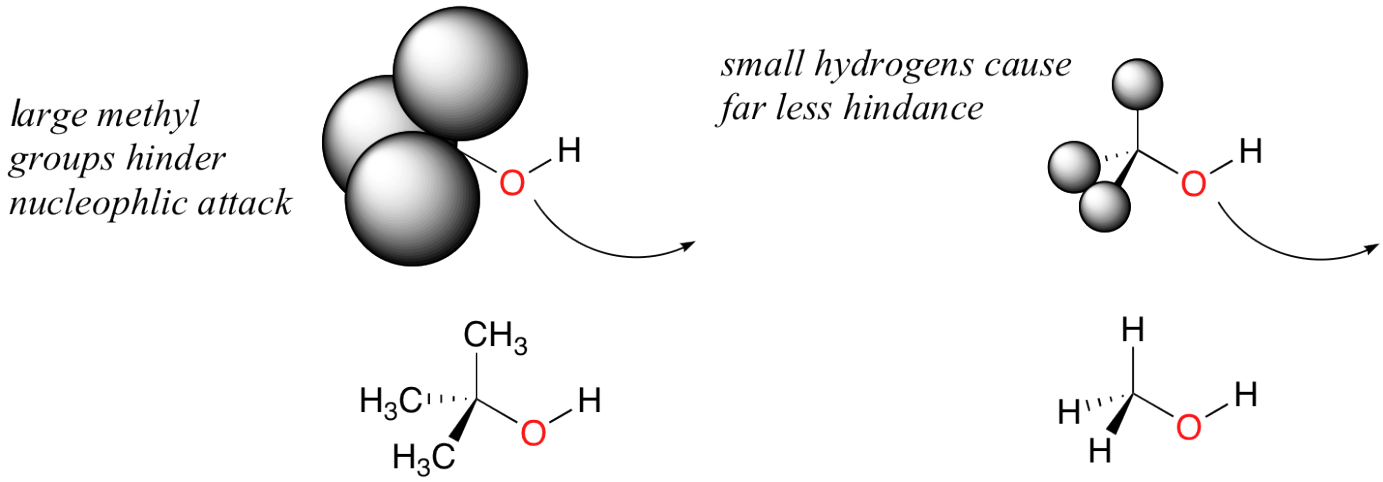
amine
more nucleophilic



amide
less nucleophilic

Steric effects on nucleophilicity

Steric hindrance is an important consideration when evaluating nucleophility. For example, *tert*-butanol is less potent as a nucleophile than methanol. This is because the comparatively bulky methyl groups on the tertiary alcohol effectively block the route of attack by the nucleophilic oxygen, slowing the reaction down considerably (imagine trying to walk through a narrow doorway while carrying three large suitcases!).



It is not surprising that it is more common to observe serines acting as nucleophiles in enzymatic reactions compared to threonines - the former is a primary alcohol, while the latter is a secondary alcohol.

Contributors and Attributions

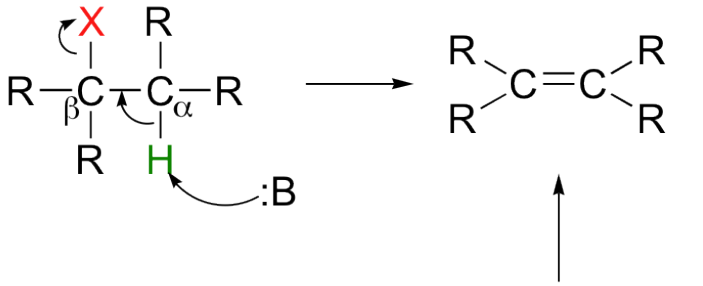
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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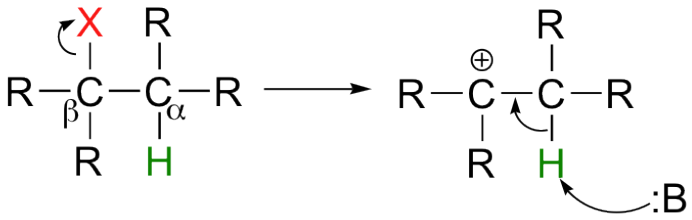
27.3: Introduction to Elimination Reactions

Elimination reactions are also possible at positions that are isolated from carbonyls or any other electron-withdrawing groups. This type of elimination can be described by two model mechanisms: it can occur in a single concerted step (proton abstraction at C_α occurring at the same time as C_β-X bond cleavage), or in two steps (C_β-X bond cleavage occurring first to form a carbocation intermediate, which is then 'quenched' by proton abstraction at the alpha-carbon).

concerted (E2) elimination



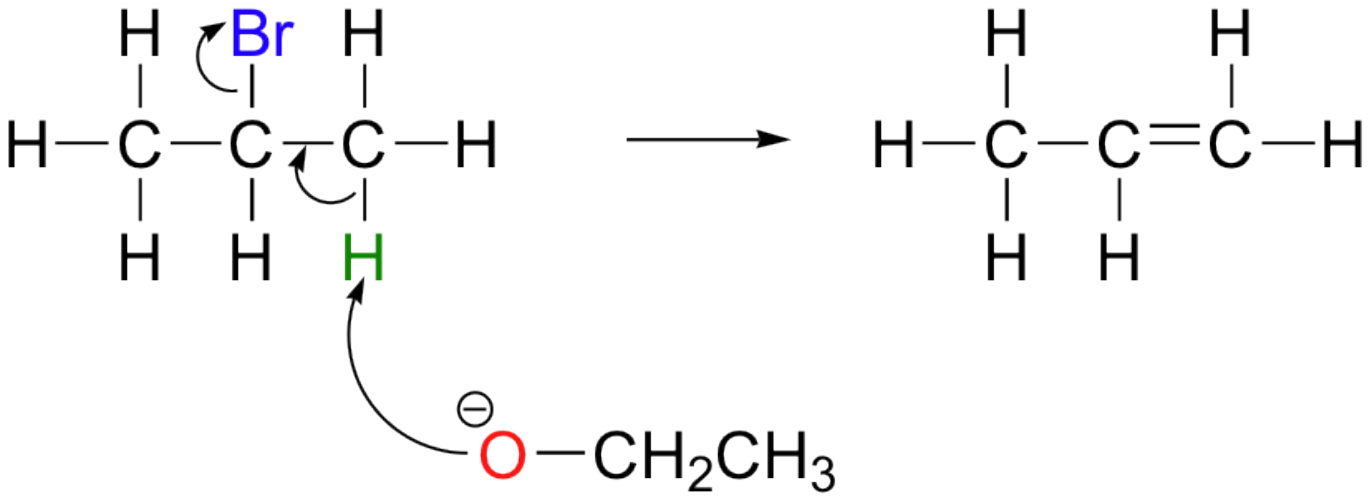
carbocation (E1) elimination



These mechanisms, termed E2 and E1, respectively, are important in laboratory organic chemistry, but are less common in biological chemistry. As explained below, which mechanism actually occurs in a laboratory reaction will depend on the identity of the R groups (ie., whether the alkyl halide is primary, secondary, tertiary, etc.) as well as on the characteristics of the base.

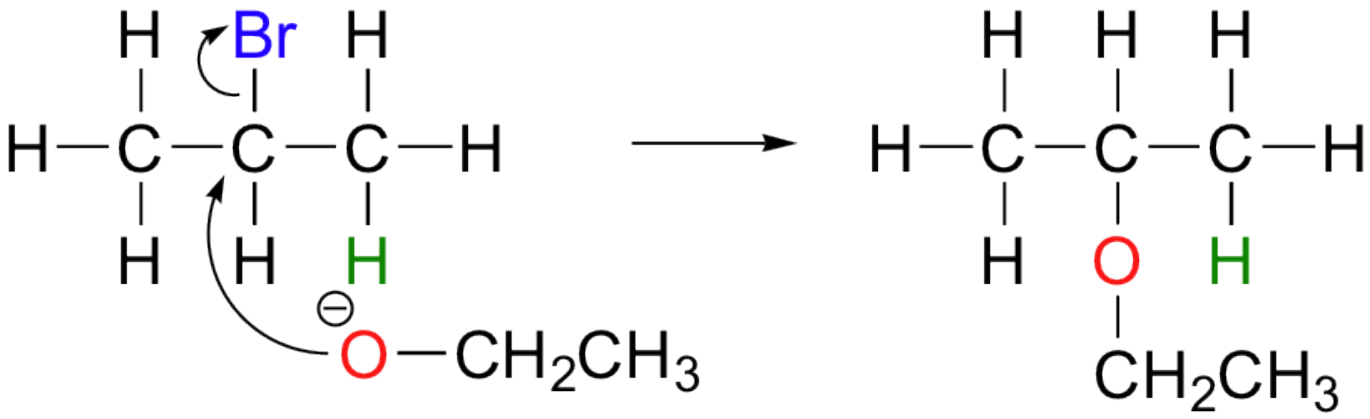
E1 and E2 reactions in the laboratory

E2 elimination reactions in the laboratory are carried out with relatively strong bases, such as alkoxides (deprotonated alcohols). 2-bromopropane will react with ethoxide, for example, to give propene.

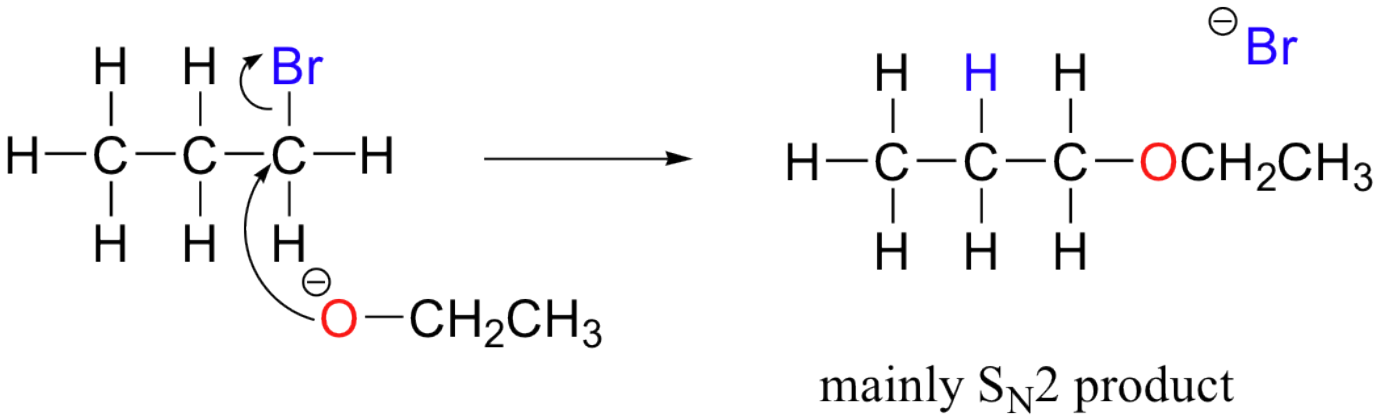


Propene is not the only product of this reaction, however - the ethoxide will also to some extent act as a nucleophile in an S_N2

reaction.

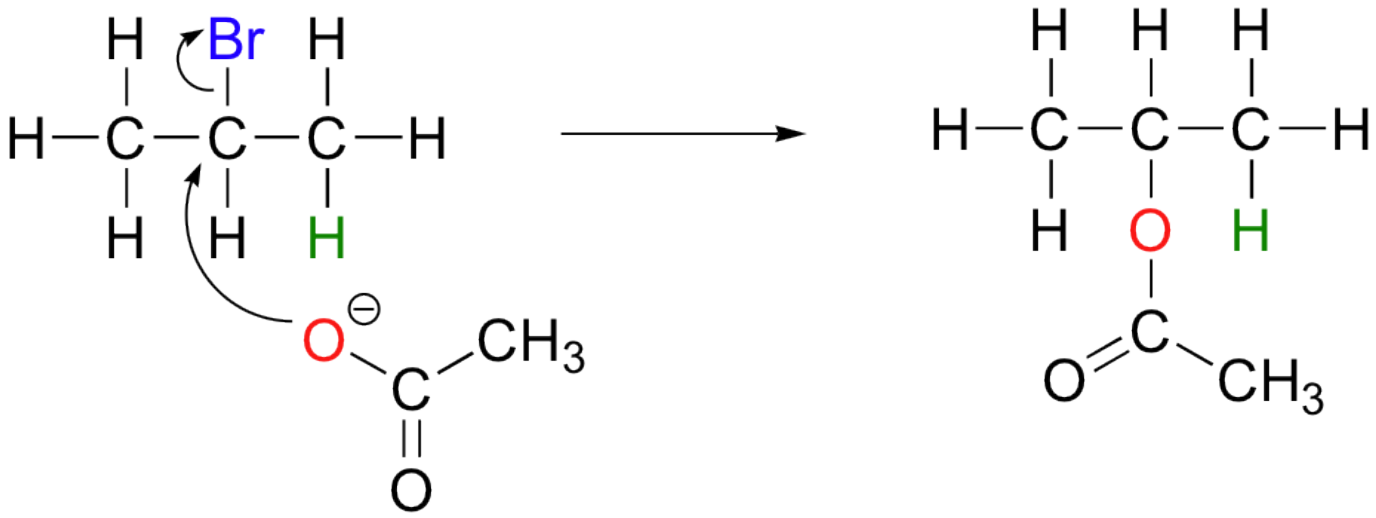


Chemists carrying out nonenzymatic nucleophilic substitution or elimination reactions always have to be aware of the competition between the two mechanisms, because bases can also be nucleophiles, and vice-versa. However, a chemist can tip the scales in one direction or another by carefully choosing reagents. Primary carbon electrophiles like 1-bromopropane, for example, are much more likely to undergo substitution (by the S_N2 mechanism) than elimination (by the E2 mechanism) – this is because the electrophilic carbon is unhindered and a good target for a nucleophile.

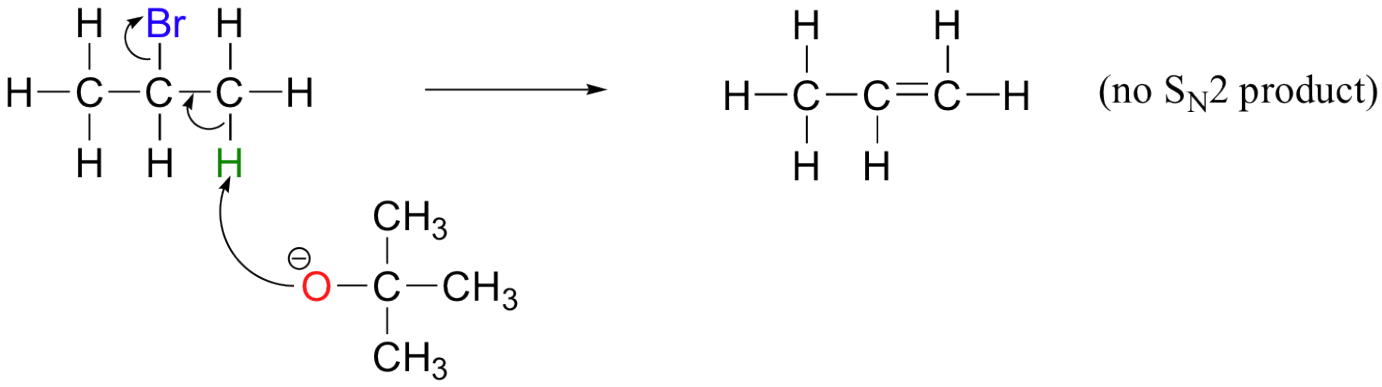


S_N1 and E1 mechanisms are unlikely with such compounds because of the relative instability of primary carbocations.

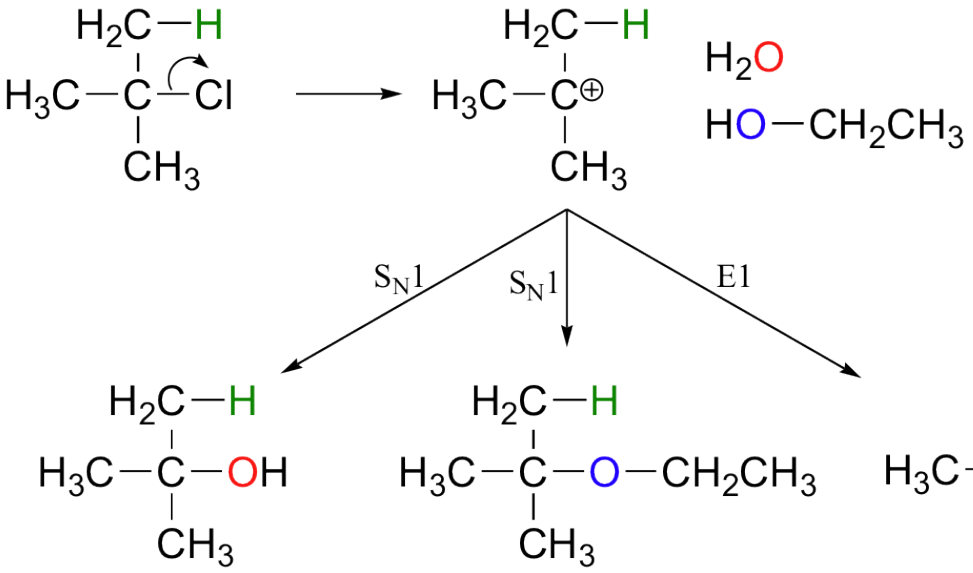
The nature of the electron-rich species is also critical. Acetate, for example, is a weak base but a reasonably good nucleophile, and will react with 2-bromopropane mainly as a nucleophile.



In order to direct the reaction towards elimination, a strong *hindered* base such as tert-butoxide can be used. The bulkiness of tert-butoxide makes it difficult for the oxygen to reach the carbon (in other words, to act as a nucleophile). It is more likely to pluck off a proton, which is much more accessible than the electrophilic carbon).



E1 reactions occur by the same kinds of carbocation-favoring conditions that have already been described for S_N1 reactions (section 9.4): a secondary or tertiary substrate, a protic solvent, and a relatively weak base/nucleophile. In fact, E1 and S_N1 reactions generally occur simultaneously, giving a mixture of substitution and elimination products after formation of a common carbocation intermediate. When tert-butyl chloride is stirred in a mixture of ethanol and water, for example, a mixture of S_N1 products (tert-butyl alcohol and tert-butyl ethyl ether) and E1 product (2-methylpropene) results.

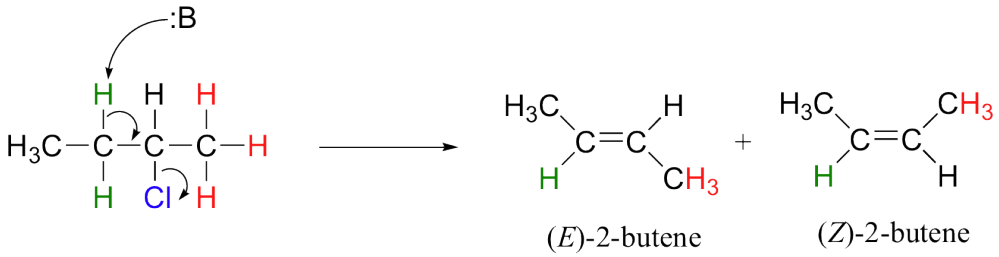


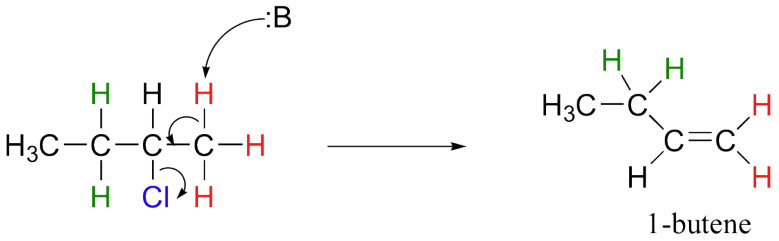
Exercise

A straightforward functional group conversion that is often carried out in the undergraduate organic lab is the phosphoric acid-catalyzed dehydration of cyclohexanol to form cyclohexene. No solvent is necessary in this reaction - pure liquid cyclohexanol is simply stirred together with a few drops of concentrated phosphoric acid. In order to drive the equilibrium of this reversible reaction towards the desired product, cyclohexene is distilled out of the reaction mixture as it forms (the boiling point of cyclohexene is 83 ^{o}C, significantly lower than that of anything else in the reaction solution). Any cyclohexyl phosphate that might form from the competing S_N1 reaction remains in the flask, and is eventually converted to cyclohexene over time. Draw a mechanism for the cyclohexene synthesis reaction described above. Also, draw a mechanism showing how the undesired cyclohexyl phosphate could form.

Solutions to exercises

Next, let's put aside the issue of competition between nucleophilic substitution and elimination, and focus on the regioselectivity of elimination reactions. In many cases an elimination reaction can result in more than one constitutional isomer or stereoisomer. The elimination products of 2-chloropentane provide a good example:

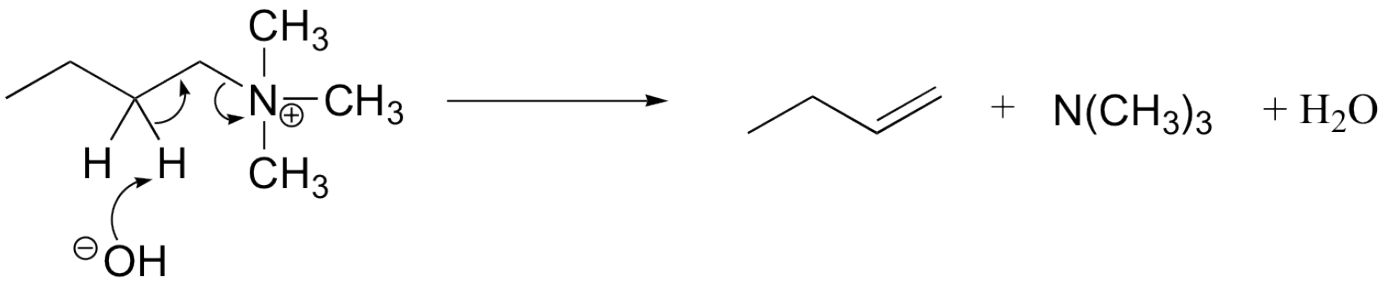




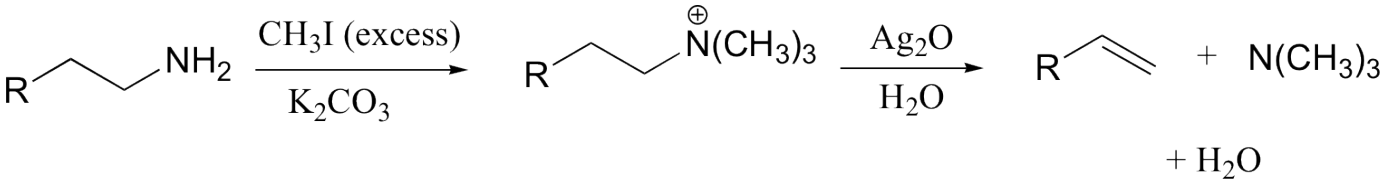
This reaction is both regiospecific and stereospecific. In general, *more substituted alkenes are more stable*, and as a result, the

product mixture will contain less 1-butene than 2-butene (this is the regiochemical aspect of the outcome, and is often referred to as **Zaitsev's rule**). In addition, we already know that *trans* (*E*) alkenes are generally more stable than *cis* (*Z*) alkenes (section 3.7C), so we can predict that more of the *E* product will form compared to the *Z* product.

The **Hoffman elimination** is a well-studied E2 elimination in which the leaving group is a quaternary amine - note that there is no proton on the quaternary amine that could protonate the base in the reaction:

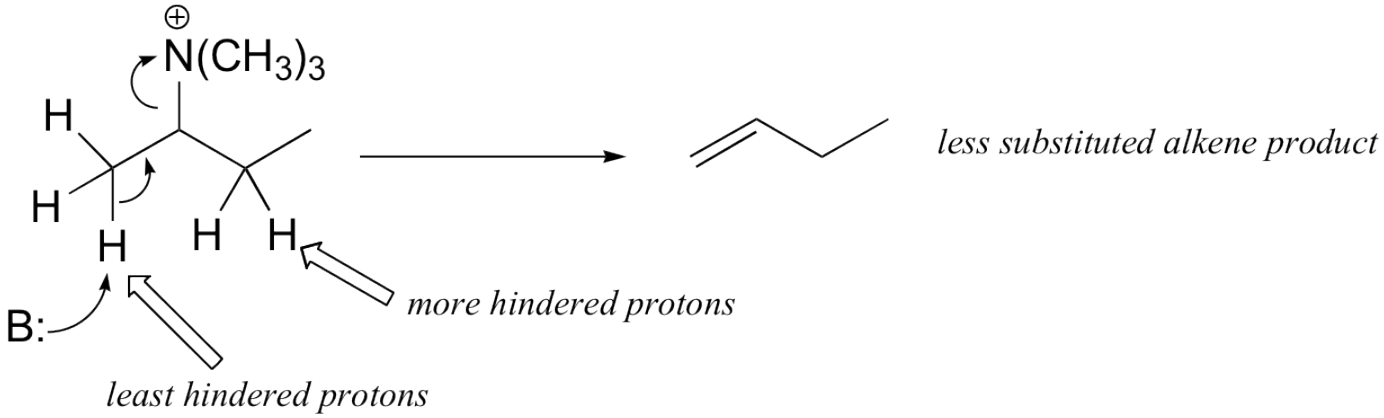


In practice, the quaternary amine is made by treating a primary or secondary amine with excess methyl iodide and weak base (this, of course, is an S_N2 methylation reaction, covered in section 9.1B). Silver oxide in water generates the necessary hydroxide ion.

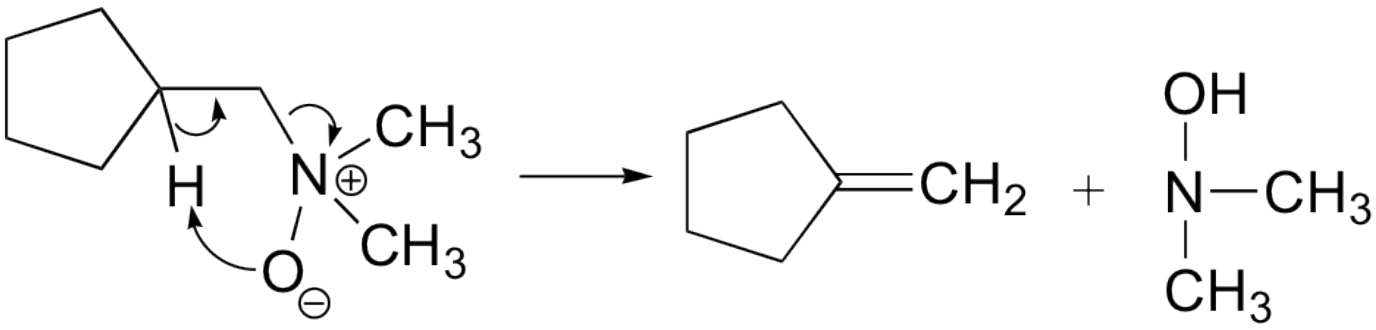


There is very little competing substitution under these conditions.

The Hoffman elimination is somewhat unique in that, unlike other elimination reactions, it is usually the *least* substituted alkene that is the predominant product. This is due to steric factors: the large size of the quaternary ammonium leaving group results in the most accessible (least hindered) proton being abstracted - meaning the proton from the least substituted carbon.



The **Cope elimination** is another well-known laboratory E2 reaction involving an amine oxide:



Notice that the leaving group is also the base. The transition state is thought to be planar (or close to it).

Contributors and Attributions

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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27.4: Reactions of Alcohols

Learning Objectives

1. Give two major types of reactions of alcohols.
2. Describe the result of the oxidation of a primary alcohol.
3. Describe the result of the oxidation of a secondary alcohol.

Chemical reactions in alcohols occur mainly at the functional group, but some involve hydrogen atoms attached to the OH-bearing carbon atom or to an adjacent carbon atom. Of the three major kinds of alcohol reactions, which are summarized in Figure 27.4.1 , two—dehydration and oxidation—are considered here. The third reaction type—esterification—is covered elsewhere.

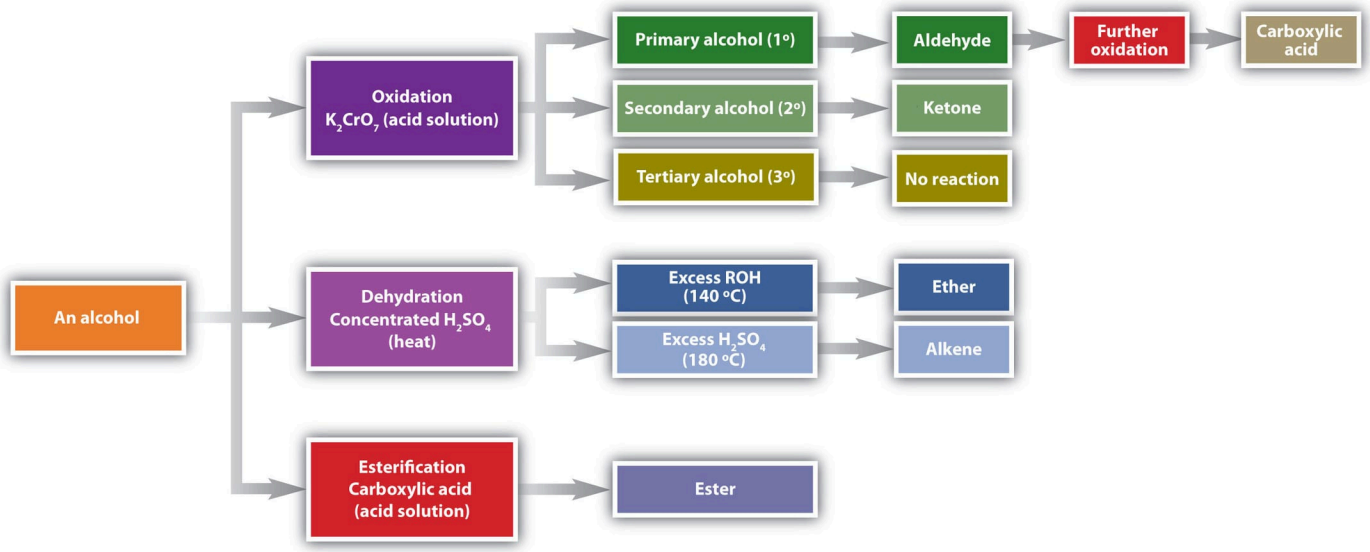
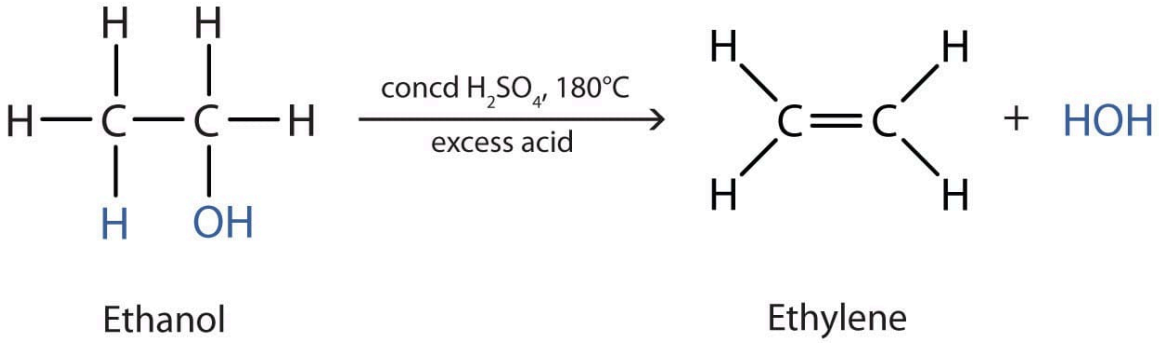


Table 27.4.1: *Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here.*

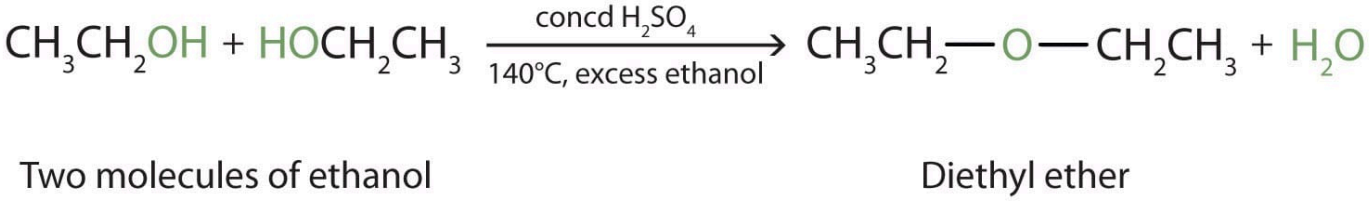
Dehydration of Alcohols

As noted in Figure 27.4.1, an alcohol undergoes dehydration in the presence of a catalyst to form an alkene and water. The reaction removes the OH group from the alcohol carbon atom and a hydrogen atom from an adjacent carbon atom in the same molecule:



Under the proper conditions, it is possible for the dehydration to occur between *two* alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached

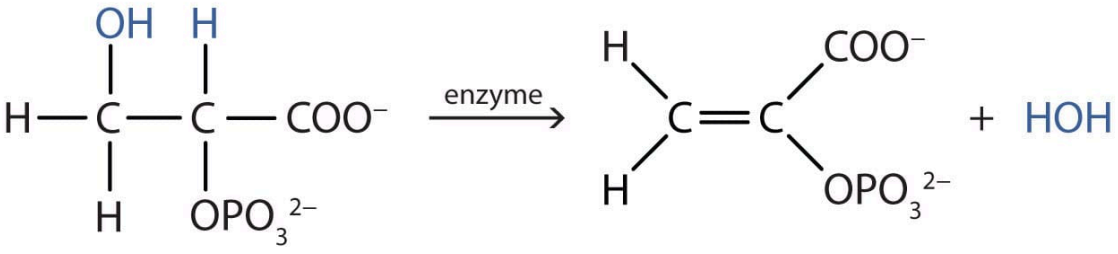
to an oxygen atom form an ether molecule.



(Ethers are discussed in elsewhere) Thus, depending on conditions, one can prepare either alkenes or ethers by the dehydration of alcohols.

Note

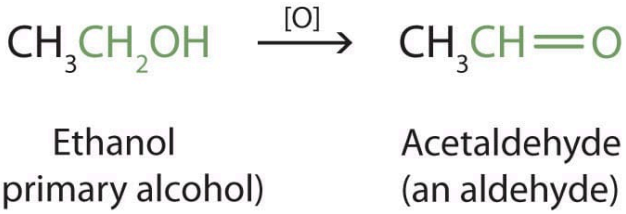
Both dehydration and hydration reactions occur continuously in cellular metabolism, with enzymes serving as catalysts and at a temperature of about 37°C. The following reaction occurs in the "Embden–Meyerhof" pathway



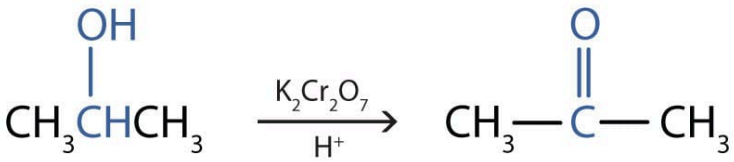
Although the participating compounds are complex, the reaction is the same: elimination of water from the starting material. The idea is that if you know the chemistry of a particular functional group, you know the chemistry of hundreds of different compounds.

Oxidation of Acohols

Primary and secondary alcohols are readily oxidized. We saw earlier how methanol and ethanol are oxidized by liver enzymes to form aldehydes. Because a variety of oxidizing agents can bring about oxidation, we can indicate an oxidizing agent without specifying a particular one by writing an equation with the symbol [O] above the arrow. For example, we write the oxidation of ethanol—a primary alcohol—to form acetaldehyde—an aldehyde—as follows:



We shall see that aldehydes are even more easily oxidized than alcohols and yield carboxylic acids. Secondary alcohols are oxidized to *ketones*. The oxidation of isopropyl alcohol by potassium dichromate ($K_2Cr_2O_7$) gives acetone, the simplest ketone:



Isopropyl alcohol
(a secondary alcohol)

Acetone
(a ketone)

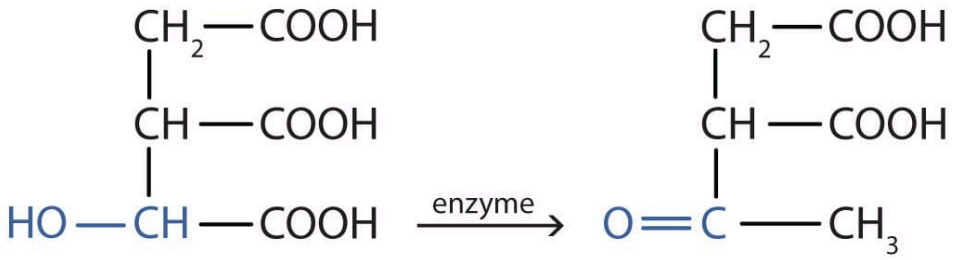
Unlike aldehydes, ketones are relatively resistant to further oxidation, so no special precautions are required to isolate them as they form. Note that in oxidation of both primary (RCH_2OH) and secondary (R_2CHOH) alcohols, two hydrogen atoms are removed from the alcohol molecule, one from the OH group and other from the carbon atom that bears the OH group.

Note

These reactions can also be carried out in the laboratory with chemical oxidizing agents. One such oxidizing agent is potassium dichromate. The balanced equation (showing only the species involved in the reaction) in this case is as follows:

$$8H^+ + Cr_2O_7^{2-} + 3CH_3CH_2OH \longrightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$$

Alcohol oxidation is important in living organisms. Enzyme-controlled oxidation reactions provide the energy cells need to do useful work. One step in the metabolism of carbohydrates involves the oxidation of the secondary alcohol group in isocitric acid to a ketone group:



Isocitrate

Oxalosuccinate

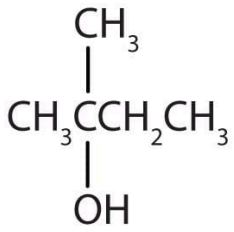
The overall type of reaction is the same as that in the conversion of isopropyl alcohol to acetone.

Tertiary alcohols (R_3COH) are resistant to oxidation because the carbon atom that carries the OH group does not have a hydrogen atom attached but is instead bonded to other carbon atoms. The oxidation reactions we have described involve the formation of a carbon-to-oxygen double bond. Thus, the carbon atom bearing the OH group must be able to release one of its attached atoms to form the double bond. The carbon-to-hydrogen bonding is easily broken under oxidative conditions, but carbon-to-carbon bonds are not. Therefore tertiary alcohols are not easily oxidized.

Example 27.4.1

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write “no reaction” after the arrow.

1. $CH_3CH_2CH_2CH_2CH_2OH$

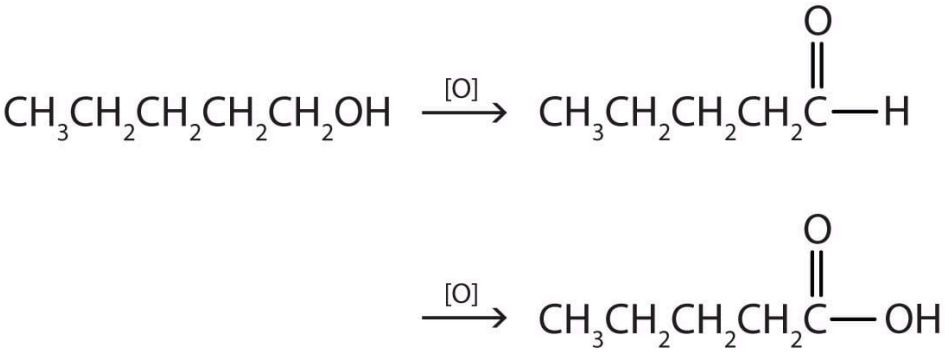
2. 

3. 

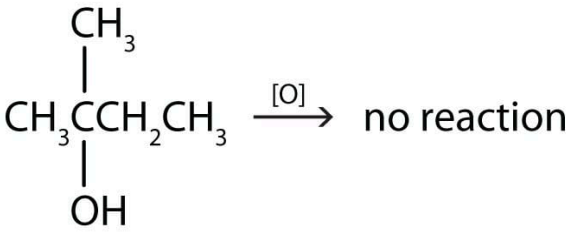
Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

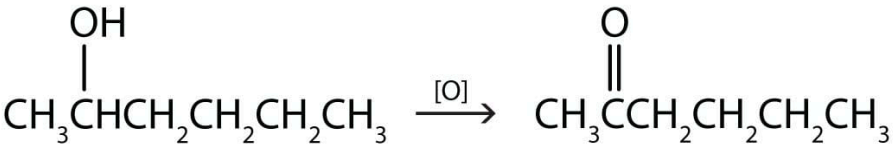
1. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.



2. This alcohol has the OH group on a carbon atom that is attached to three other carbon atoms, so it is a tertiary alcohol. No reaction occurs.

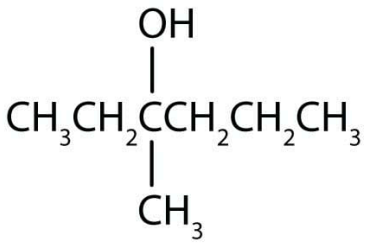
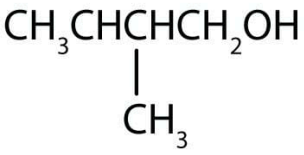
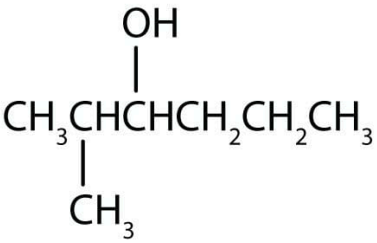


3. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol; oxidation gives a ketone.



Exercise 27.4.1

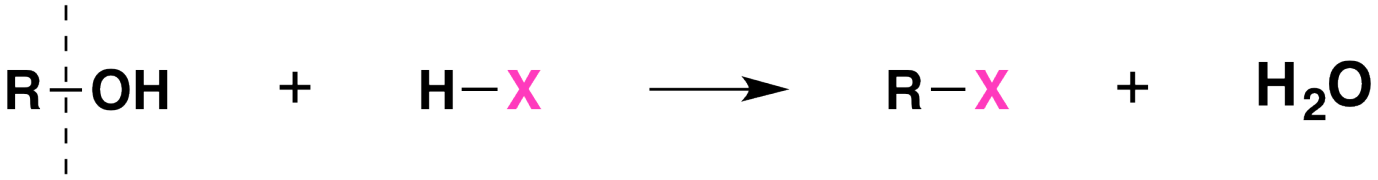
Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write “no reaction” after the arrow.

1. 
2. 
3. 

Reactions of Alcohols with Hydrogen Halides (HX)

/Organic_Chemistry/Alcohols/Reactions_of_Alcohols/Reactions_of_alcohols_with_hydrohalic_acids_(HX)

When alcohols react with a hydrogen halide, a substitution occurs, producing an alkyl halide and water:



Scope of Reaction

- The order of reactivity of alcohols is 3° > 2° > 1° methyl.
- The order of reactivity of the hydrogen halides is HI > HBr > HCl (HF is generally unreactive).

The reaction is acid catalyzed. Alcohols react with the strongly acidic hydrogen halides HCl, HBr, and HI, but they do not react with nonacidic NaCl, NaBr, or NaI. Primary and secondary alcohols can be converted to alkyl chlorides and bromides by allowing them to react with a mixture of a sodium halide and sulfuric acid:

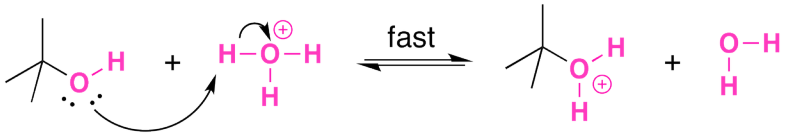


Mechanisms of the Reactions of Alcohols with HX

Secondary, tertiary, allylic, and benzylic alcohols appear to react by a mechanism that involves the formation of a carbocation in an S_N1 reaction with the protonated alcohol acting as the substrate.

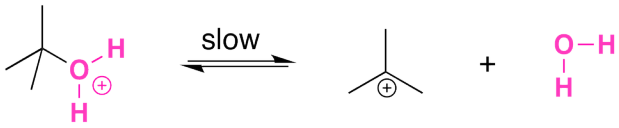
The S_N1 mechanism is illustrated by the reaction tert-butyl alcohol and aqueous hydrochloric acid (H_3O^+, Cl^-). The first two steps in this S_n1 substitution mechanism are protonation of the alcohol to form an oxonium ion. Although the oxonium ion is formed by protonation of the alcohol, it can also be viewed as a Lewis acid-base complex between the cation (R^+) and H_2O. Protonation of the alcohol converts a poor leaving group (OH-) to a good leaving group (\)H_2O_), which makes the dissociation step of the S_N1 mechanism more favorable.

Step 1



the alcohol accepts a proton

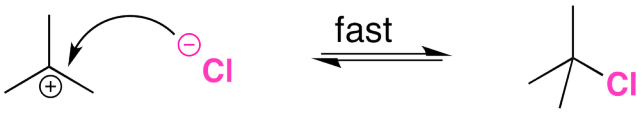
Step 2



the protonated hydroxyl group departs as a leaving group to form a carbocation and water

In step 3, the carbocation reacts with a nucleophile (a halide ion) to complete the substitution.

Step 3



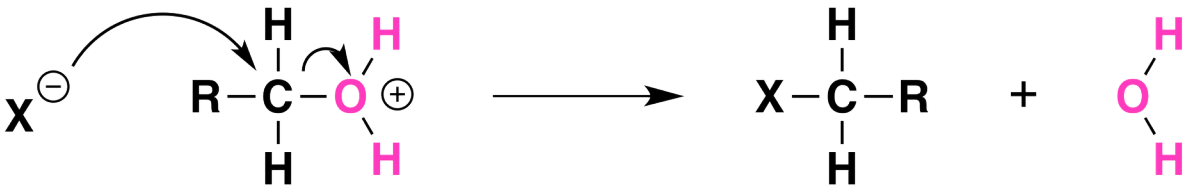
a halide anion reacts with the carbocation

When we convert an alcohol to an alkyl halide, we perform the reaction in the presence of acid and in the presence of halide ions and not at elevated temperatures. Halide ions are good nucleophiles (they are much stronger nucleophiles than water), and because halide ions are present in a high concentration, most of the carbocations react with an electron pair of a halide ion to form a more stable species, the alkyl halide product. The overall result is an S_n1 reaction.

Primary Alcohols

Not all acid-catalyzed conversions of alcohols to alkyl halides proceed through the formation of carbocations. Primary alcohols and methanol react to form alkyl halides under acidic conditions by an S_N2 mechanism.

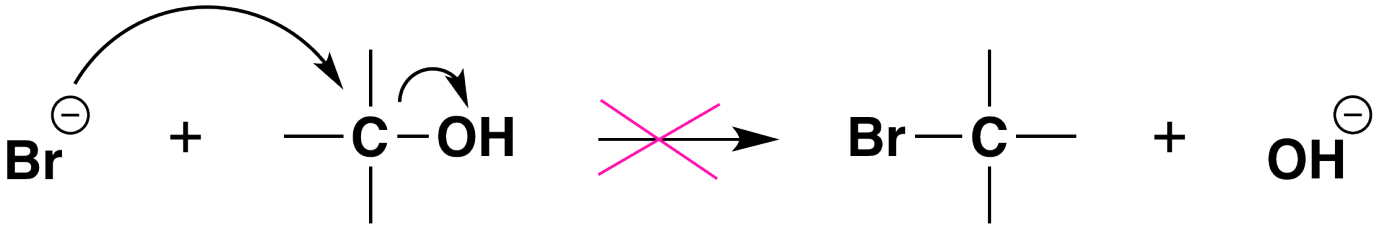
In these reactions, the function of the acid is to produce a *protonated alcohol*. The halide ion then displaces a molecule of water (a good leaving group) from carbon; this produces an alkyl halide:



(protonated 1° alcohol or methanol)

(A good leaving group)

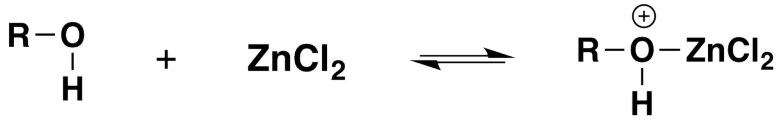
Again, acid is required. Although halide ions (particularly iodide and bromide ions) are strong nucleophiles, they are not strong enough to carry out substitution reactions with alcohols themselves. Direct displacement of the hydroxyl group does not occur because the leaving group would have to be a strongly basic hydroxide ion:

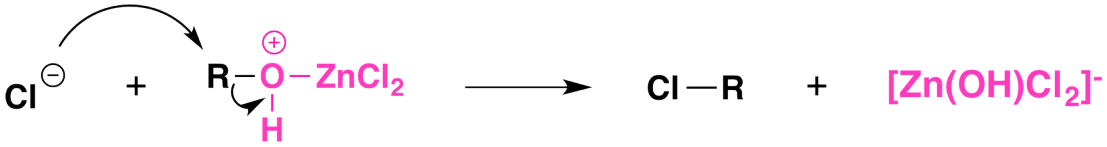


We can see now why the reactions of alcohols with hydrogen halides are acid-promoted.

The role of acid catalysis

Acid protonates the alcohol hydroxyl group, making it a good leaving group. However, other strong Lewis acids can be used instead of hydrohalic acids. Because the chloride ion is a weaker nucleophile than bromide or iodide ions, hydrogen chloride does not react with primary or secondary alcohols unless zinc chloride or a similar Lewis acid is added to the reaction mixture as well. Zinc chloride, a good Lewis acid, forms a complex with the alcohol through association with an unshared pair of electrons on the oxygen atom. This enhances the hydroxyl's leaving group potential sufficiently so that chloride can displace it.







Rearrangement

As we might expect, many reactions of alcohols with hydrogen halides, particularly those in which carbocations are formed, are accompanied by rearrangements. The general rule is that if rearrangement CAN OCCUR (to form more stable or equally stable cations), it will! In these reactions, mixtures of products can be formed.

Contributors

- Prof. Paul G. Wenthold (Purdue University)

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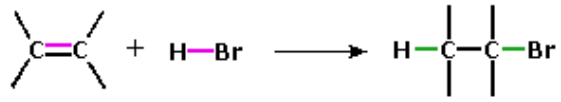
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27.5: Introduction to Addition Reactions: Reactions of Alkenes

The most common chemical transformation of a carbon-carbon double bond is the **addition reaction**. A large number of reagents, both inorganic and organic, have been found to add to this functional group, and in this section we shall review many of these reactions.

- Addition of Lewis Acids (Electrophilic Reagents)
- Addition of Strong Brønsted Acids
- Rearrangement of Carbocations

A large number of reagents, both inorganic and organic, have been found to add to this functional group, and in this section we shall review many of these reactions. A majority of these reactions are exothermic, due to the fact that the C-C pi-bond is relatively weak (ca. 63 kcal/mole) compared to the sigma-bonds formed with the atoms or groups of the reagent. Remember, the bond energies of a molecule are the energies required to break (homolytically) all the covalent bonds in the molecule. Consequently, if the bond energies of the product molecules are greater than the bond energies of the reactants, the reaction will be exothermic. The following calculations for the addition of H-Br are typical. Note that by convention exothermic reactions have a negative heat of reaction.



Heat of Reaction = 150.5 − 167.0 = −16.5 kcal/mole

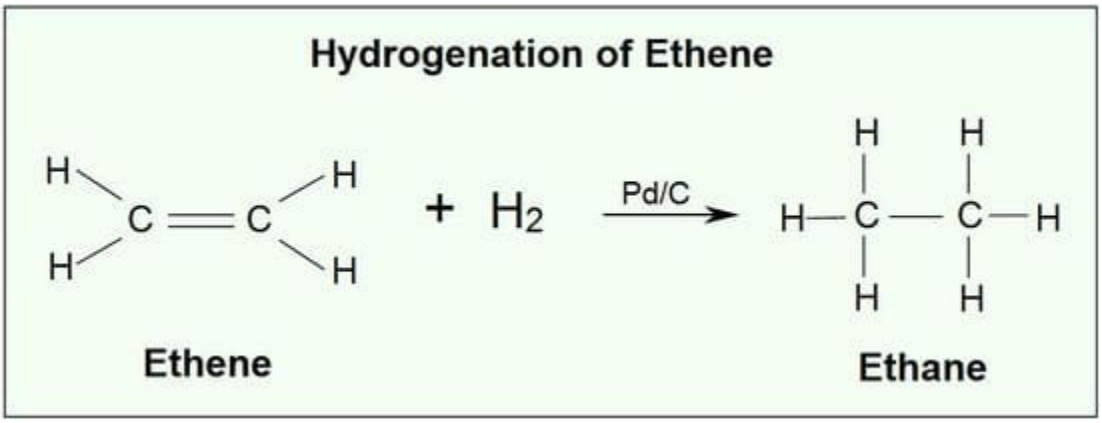
Bonds Broken: πC=C & H–Br Sum = 150.5 kcal/mole
63 87.5

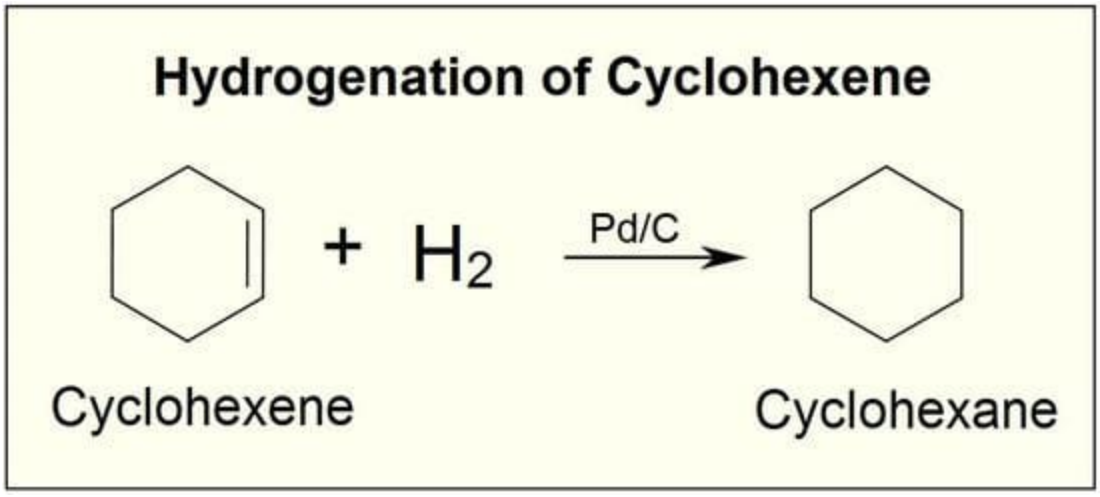
Bonds Formed: H–C & Br–C Sum = 167.0 kcal/mole
99 68

Addition of Hydrogen: Hydrogenation of Alkenes

Addition of hydrogen to a carbon-carbon double bond is called hydrogenation. The overall effect of such an addition is the reductive removal of the double bond functional group. Regioselectivity is not an issue, since the same group (a hydrogen atom) is bonded to each of the double bond carbons. The simplest source of two hydrogen atoms is molecular hydrogen (H_2), but mixing alkenes with hydrogen does not result in any discernible reaction. Although the overall hydrogenation reaction is exothermic, a high activation energy prevents it from taking place under normal conditions. This restriction may be circumvented by the use of a catalyst,

Ethene reacts with hydrogen in the presence of a finely divided palladium catalyst at a temperature of about 150°C. Ethane is produced.





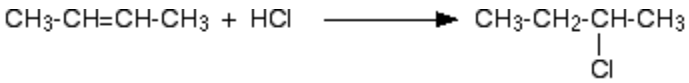
This is a fairly pointless reaction because ethene is a far more useful compound than ethane! However, what is true of the reaction of the carbon-carbon double bond in ethene is equally true of it in much more complicated cases.

Addition of Hydrogen Halides to Alkenes

All alkenes undergo addition reactions with the hydrogen halides. A hydrogen atom joins to one of the carbon atoms originally in the double bond, and a halogen atom to the other. For example, with ethene and hydrogen chloride, you get chloroethane:



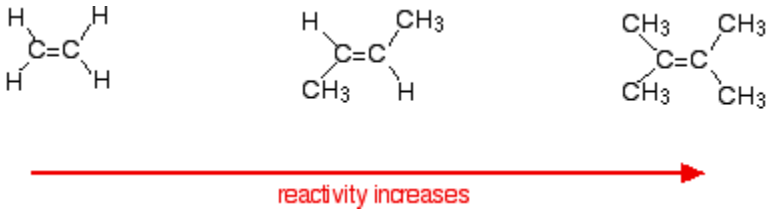
With but-2-ene you get 2-chlorobutane:



What happens if you add the hydrogen to the carbon atom at the right-hand end of the double bond, and the chlorine to the left-hand end? You would still have the same product. The chlorine would be on a carbon atom next to the end of the chain - you would simply have drawn the molecule flipped over in space. That would be different of the alkene was unsymmetrical - that's why we have to look at them separately.

Reaction rates increase in the order HF - HCl - HBr - HI. Hydrogen fluoride reacts much more slowly than the other three, and is normally ignored in talking about these reactions. When the hydrogen halides react with alkenes, the hydrogen-halogen bond has to be broken. The bond strength falls as you go from HF to HI, and the hydrogen-fluorine bond is particularly strong. Because it is difficult to break the bond between the hydrogen and the fluorine, the addition of HF is bound to be slow.

This applies to unsymmetrical alkenes as well as to symmetrical ones. For simplicity the examples given below are all symmetrical ones- but they don't have to be. Reaction rates increase as the alkene gets more complicated - in the sense of the number of alkyl groups (such as methyl groups) attached to the carbon atoms at either end of the double bond. For example:

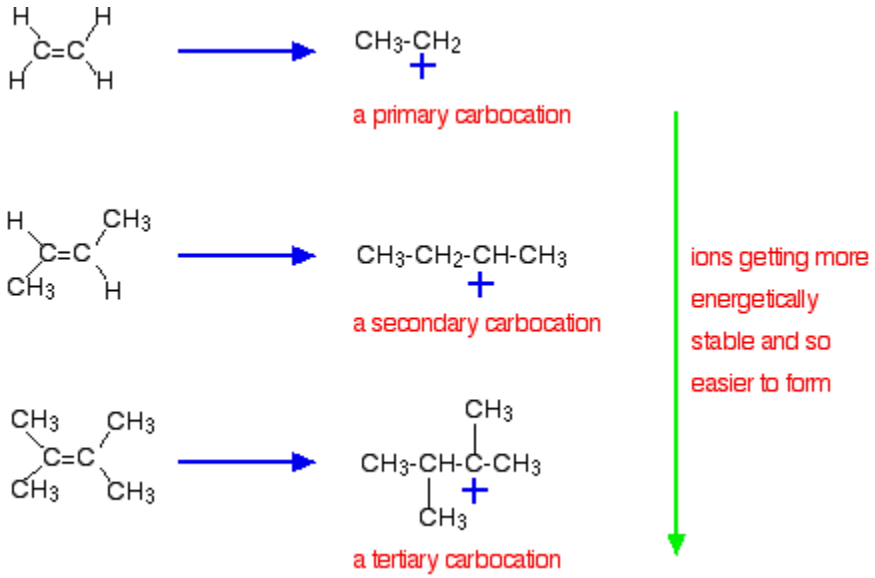


There are two ways of looking at the reasons for this - both of which need you to know about the mechanism for the reactions.

Alkenes react because the electrons in the pi bond attract things with any degree of positive charge. Anything which increases the electron density around the double bond will help this. Alkyl groups have a tendency to "push" electrons away from themselves towards the double

bond. The more alkyl groups you have, the more negative the area around the double bonds becomes. The more negatively charged that region becomes, the more it will attract molecules like hydrogen chloride.

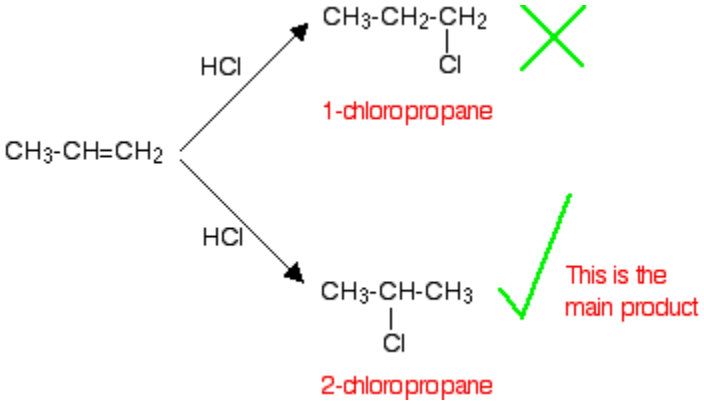
The more important reason, though, lies in the stability of the intermediate ion formed during the reaction. The three examples given above produce these carbocations (carbonium ions) at the half-way stage of the reaction:



The stability of the intermediate ions governs the activation energy for the reaction. As you go towards the more complicated alkenes, the activation energy for the reaction falls. That means that the reactions become faster.

Addition to unsymmetrical alkenes

In terms of reaction conditions and the factors affecting the rates of the reaction, there is no difference whatsoever between these alkenes and the symmetrical ones described above. The problem comes with the orientation of the addition - in other words, which way around the hydrogen and the halogen add across the double bond. If HCl adds to an unsymmetrical alkene like propene, there are two possible ways it could add. However, in practice, there is only one major product.



This is in line with Markovnikov's Rule.

Definition: Markovnikov's Rule

When a compound HX is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already.

In this case, the hydrogen becomes attached to the CH_2 group, because the CH_2 group has more hydrogens than the CH group. Notice that only the hydrogens directly attached to the carbon atoms at either end of the double bond count. The ones in the CH_3 group are totally irrelevant.

Addition of Halogens: Halogenation of Alkenes

As halogen molecule, for example Br_2, approaches a double bond of the alkene, electrons in the double bond repel electrons in bromine molecule causing polarization of the halogen bond. This creates a dipolar moment in the halogen molecule bond. Heterolytic bond cleavage occurs and one of the halogens obtains positive charge and reacts as an electrophile. The reaction of the addition is not regioselective but stereoselective.Stereochemistry of this addition can be explained by the mechanism of the reaction.In the first step electrophilic halogen with a positive charge approaches the double carbon bond and 2 p orbitals of the halogen, bond with two carbon atoms and create a cyclic ion with a halogen as the intermediate step. In the second step, halogen with the negative charge attacks any of the two carbons in the cyclic ion from the back side of the cycle as in the S_N2 reaction. Therefore stereochemistry of the product is **vicinial dihalides through anti** addition.

$$\mathrm{R_2C{=}CR_2 + X_2 \ \rightarrow R_2CX{-}CR_2X} \tag{27.5.1}$$

Halogens that are commonly used in this type of the reaction are: Br and Cl. In thermodynamical terms I is too slow for this reaction because of the size of its atom, and F is too vigorous and explosive. Solvents that are used for this type of electrophilic halogenation are inert (e.g., CCl_4) can be used in this reaction. Because halogen with negative charge can attack any carbon from the opposite side of the cycle it creates a mixture of steric products.

Electrophilic addition mechanism consists of two steps. Before constructing the mechanism let us summarize conditions for this reaction. We will use Br_2 in our example for halogenation of ethylene.

Nucleophile	**Double bond in alkene**
Electrophile	Br_2, Cl_2
Regiochemistry	not relevant
Stereochemistry	**ANTI**

Step 1: In the first step of the addition the Br-Br bond polarizes, heterolytic cleavage occurs and Br with the positive charge forms a intermediate cycle with the double bond.

Mechanism1.bmp

Step 2: In the second step, bromide anion attacks any carbon of the bridged bromonium ion from the back side of the cycle. Cycle opens up and two halogens are in the position **anti**.

Mechanism 2 a.bmp

Contributors and Attributions

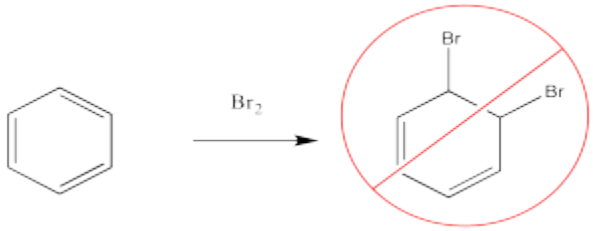
- Jim Clark (Chemguide.co.uk)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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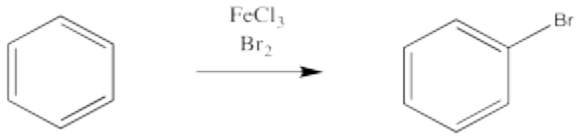
27.6: Electrophilic Aromatic Substitution

Aromatics, or arenes, are derivatives of benzene or other compounds with aromatic ring systems. That is, they are cyclic, planar, fully conjugated and have an odd number of π-electron pairs. Like alkenes, aromatics have π-electrons that are loosely held and are easily attracted to electrophiles. However, aromatics don't undergo the typical reactions of alkenes.

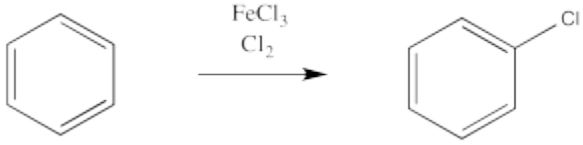
For example, bromine will not add across the double bond of benzene.



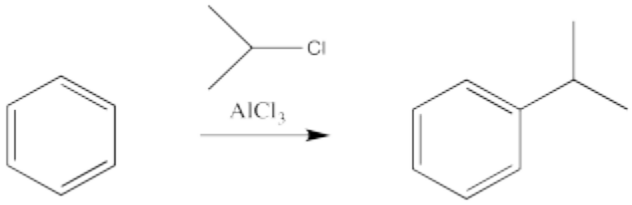
Instead, a bromine atom replaces one of the hydrogen atoms on the benzene. This reaction is greatly accelerated in the presence of Lewis acids, such as ferric chloride.



A similar reaction happens with chlorine. If treated with chlorine gas and a metal catalyst, a chlorine atom from chlorine gas can replace a hydrogen atom on benzene. However, the same thing doesn't work as smoothly with the other halogens, iodine and fluorine.

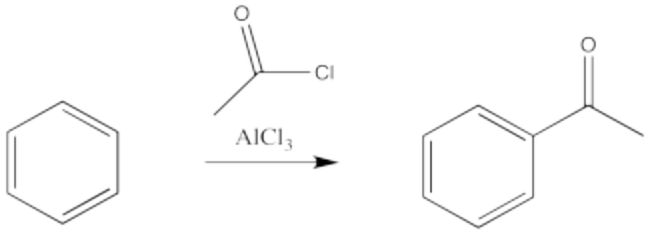


The reactions of chlorine and bromine with benzene and other aromatics can be catalysed by a variety of Lewis acidic metal catalysts. So can the reactions of alkyl halides and acyl halides, which we don't normally think of as electrophiles for alkene addition.



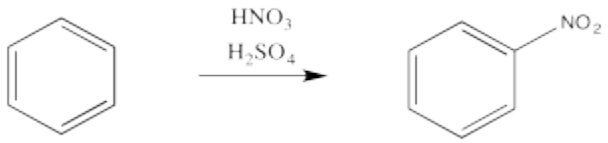
There are some limitations on what kind of groups can be added in this way. The carbon attached to the halide should be tetrahedral. Typically, it is much easier to add secondary or tertiary alkyls than primary ones. That is, the carbon attached to the halogen had best be attached to two or three other carbons as well. Methyls are very, very difficult to add in this way.

There is an exception - the carbon attached to the halogen need not be tetrahedral, provided it is a carbonyl carbon. That reaction is called an acylation.

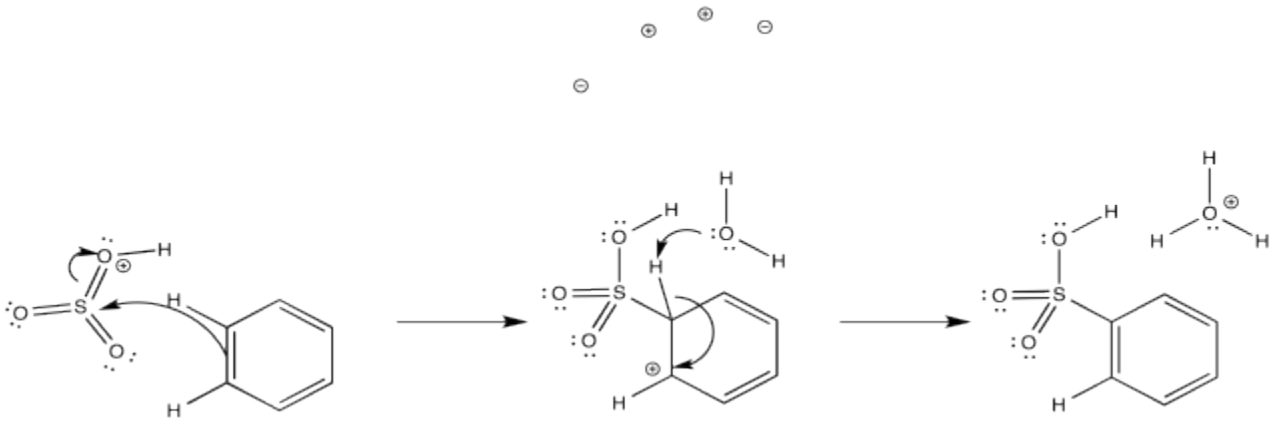


In these cases, it is the alkyl or acyl, rather than the halogen, that replaces a hydrogen atom on the benzene. Remember, benzene is most likely acting as a nucleophile in this reaction, even though it is following a different pathway than an alkene would. It is reacting with the most electrophilic part of the alkyl halide or acyl halide.

Aromatics have a limited repertoire of electrophiles with which they commonly undergo reaction. In addition to these Lewis acid-catalysed reactions, there are also reactions strong acidic media, such as a mixture of nitric and sulfuric acid.



Another acidic medium, referred to as "fuming sulfuric acid," is really a mixture of sulfuric acid and sulfur trioxide.



Just as with the acid-catalyzed reactions, the nitro group and the sulfonate group just replace a hydrogen atom on the benzene ring. The overall reaction involves bond formation between a benzene carbon and the electrophile, and bond cleavage between the same carbon and a proton.

Activation and Deactivation and Directing Effects

Because the benzene acts as a nucleophile in electrophilic aromatic substitution, substituents that make the benzene more electron-rich can accelerate the reaction. Substituents that make the benzene moor electron-poor can retard the reaction. In the mid-twentieth century, physical organic chemists including Christopher Ingold conducted a number of kinetic studies on electrophilic aromatic substitution reactions. In table 1, you can see that some substituents confer a rate of reaction that is much higher than that of benzene (R = H). Phenol, C_6H_5OH, undergoes nitration a thousand times faster than benzene does. Nitrobenzene, $C_6H_5NO_2$, undergoes the reaction millions of times more slowly.

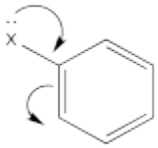
Table 27.6.1: Rate of nitration in benzene derivatives

R in C_6H_5R	Relative rate
OH	1,000
CH_3	25

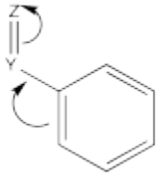
H	1
CH_2Cl	0.71
I	0.18
F	0.15
Cl	0.033
Br	0.030
CO_2Et	0.0037
NO_2	6×10^{-8}
NMe_3^+	1.2×10^{-8}

These observations are consistent with the role of the aromatic as a nucleophile in this reaction. Substituents that draw electron density away from the aromatic ring slow the reaction down. These groups are called deactivating groups in this reaction. Substituents that readily donate electron desnity to the ring, or that effectively stabilize the cationic intermediate, promote the reaction. These groups are called activating groups in this reaction.

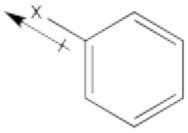
The roles of these groups are related to their electronic interactions with the electrons in the ring. Some groups might be π-donors, providing additional electron density to the benzene ring via conjugation.



Other groups may be π-acceptors, drawing electron density away from the ring via conjugation.



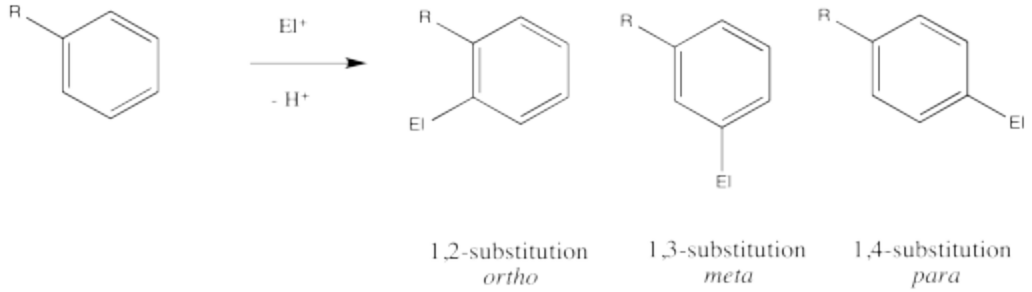
Still others may be σ-acceptors, drawing electron density away from the ring via a simple inductive effect which arises from the electronegativity of a substituent.



In some cases, there may be multiple effects, and the overall influence of the substituents is determined by the balance of the effects. One effect may be stronger in one case than the other, so it wins out in one case and loses in another.

In addition to exerting an effect on the speed of reaction, substituents on the benzene ring also influence the regiochemistry of the reaction. That is, they control *where* the new substituent appears in the product.

Remember, there are three different position on the bezene ring where a new substituent can attach, relative to the original substituent. Substitution could actually occur on five positions around the ring, but two pairs are related by symmetry. Isomerism in disubstituted benzenes can be described by numbering the substituents (1,2- etc) or by the relationships *ortho*-, *meta*- and *para*-. There are two positions *ortho*- to the initial substituent and two positions *meta*- to it.



Ingold and colleagues investigated the question of regiochemistry in nitration. They reported the following observations:

Table 27.6.2 *: Substitution patterns during nitration of benzene derivatives*

R in C_6H_5R	% *o*- product	% *m*- product	% *p*- product
CH_3	56	3	41
Cl	30	0	70
Br	38	0	62
OH	10	0	90
CHO	19	72	9
CO_2Et	28	68	3
CN	17	81	2
NO_2	6	94	0

In looking at the table, you might see that there are two groups of substituents. One group reacts to make mixtures of *ortho*- and *para*- products. There may be different ratios of *ortho*- to *para*- and there may be small amounts of *meta*-, but don't get bogged down in the details. Focus on the bigger picture. Some groups are "*ortho*-/*para*-directors".

The other group reacts to makemostly *meta*-substituted products. Here may be small amounts of*ortho*- and *para*- products, but don't worry about that. Focus on the bigger picture. Some groups are "*meta*-directors". These regiochemical effects are very closely related to the activating and directing effects we have already seen. If we want to understand this data, we need to think about things like π-donation, π-acceptance, inductive effects and cation stability.

Contributors and Attributions

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27.7: Reactions of Alkanes

Alkanes (the most basic of all organic compounds) undergo very few reactions. The two reactions of more importaces is combustion and halogenation, (i.e., substitution of a single hydrogen on the alkane for a single halogen) to form a haloalkane. The halogen reaction is very important in organic chemistry because it opens a gateway to further chemical reactions.

Combustion

Complete combustion (given sufficient oxygen) of any hydrocarbon produces carbon dioxide and water. It is quite important that you can write properly balanced equations for these reactions, because they often come up as a part of thermochemistry calculations. Some are easier than others. For example, with alkanes, the ones with an even number of carbon atoms are marginally harder than those with an odd number!

Example 27.7.1: Propane Combustion

For example, with propane (C_3H_8), you can balance the carbons and hydrogens as you write the equation down. Your first draft would be:

$$C_3H_8 + O_2 \rightarrow 3CO_2 + 4H_2O \tag{27.7.1}$$

Counting the oxygens leads directly to the final version:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \tag{27.7.2}$$

Example 27.7.2: Butane Combustion

With butane (C_4H_{10}), you can again balance the carbons and hydrogens as you write the equation down.

$$C_4H_{10} + O_2 \rightarrow 4CO_2 + 5H_2O \tag{27.7.3}$$

Counting the oxygens leads to a slight problem - with 13 on the right-hand side. The simple trick is to allow yourself to have "six-and-a-half" O_2 molecules on the left.

$$C_4H_{10} + 6\frac{1}{2}\,O_2 \rightarrow 4CO_2 + 5H_2O \tag{27.7.4}$$

If that offends you, double everything:

$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O \tag{27.7.5}$$

The hydrocarbons become harder to ignite as the molecules get bigger. This is because the bigger molecules don't vaporize so easily - the reaction is much better if the oxygen and the hydrocarbon are well mixed as gases. If the liquid is not very volatile, only those molecules on the surface can react with the oxygen. Bigger molecules have greater Van der Waals attractions which makes it more difficult for them to break away from their neighbors and turn to a gas.

Provided the combustion is complete, all the hydrocarbons will burn with a blue flame. However, combustion tends to be less complete as the number of carbon atoms in the molecules rises. That means that the bigger the hydrocarbon, the more likely you are to get a yellow, smoky flame. Incomplete combustion (where there is not enough oxygen present) can lead to the formation of carbon or carbon monoxide. As a simple way of thinking about it, the hydrogen in the hydrocarbon gets the first chance at the oxygen, and the carbon gets whatever is left over! The presence of glowing carbon particles in a flame turns it yellow, and black carbon is often visible in the smoke. Carbon monoxide is produced as a colorless poisonous gas.

Note: Why carbon monoxide is poisonous

Oxygen is carried around the blood by hemoglobin, which unfortunately binds to exactly the same site on the hemoglobin that oxygen does. The difference is that carbon monoxide binds irreversibly (or very strongly) - making that particular molecule of hemoglobin useless for carrying oxygen. If you breath in enough carbon monoxide you will die from a sort of internal suffocation.

Halogenation of Alkanes

Halogenation is the replacement of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine or iodine). Unlike the complex transformations of combustion, the halogenation of an alkane appears to be a simple **substitution reaction** in which a C-H bond is broken and a new C-X bond is formed. The chlorination of methane, shown below, provides a simple example of this reaction.

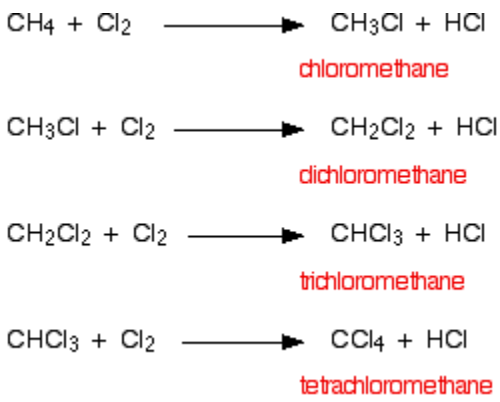
$CH_4 + Cl_2 + \text{energy} \rightarrow CH_3Cl + HCl$

Since only two covalent bonds are broken (C-H & Cl-Cl) and two covalent bonds are formed (C-Cl & H-Cl), this reaction seems to be an ideal case for mechanistic investigation and speculation. However, one complication is that all the hydrogen atoms of an alkane may undergo substitution, resulting in a mixture of products, as shown in the following unbalanced equation. The relative amounts of the various products depend on the proportion of the two reactants used. In the case of methane, a large excess of the hydrocarbon favors formation of methyl chloride as the chief product; whereas, an excess of chlorine favors formation of chloroform and carbon tetrachloride.

$$CH_4 + Cl_2 + \text{energy} \rightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$$

In the presence of a flame, the reactions are rather like the fluorine one - producing a mixture of carbon and the hydrogen halide. The violence of the reaction drops considerably as you go from fluorine to chlorine to bromine. The interesting reactions happen in the presence of ultra-violet light (sunlight will do). These are photochemical reactions that happen at room temperature. We'll look at the reactions with chlorine, although the reactions with bromine are similar, but evolve more slowly.

Substitution reactions happen in which hydrogen atoms in the methane are replaced one at a time by chlorine atoms. You end up with a mixture of chloromethane, dichloromethane, trichloromethane and tetrachloromethane.

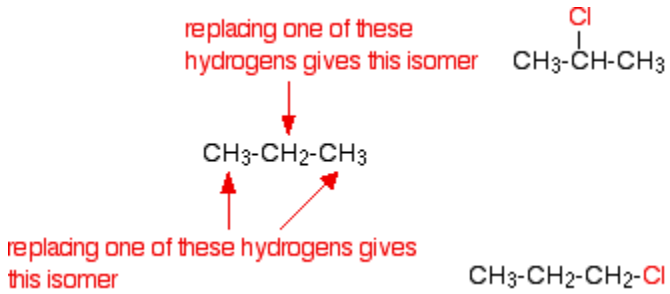


The original mixture of a colorless and a green gas would produce steamy fumes of hydrogen chloride and a mist of organic liquids. All of the organic products are liquid at room temperature with the exception of the chloromethane which is a gas.

If you were using bromine, you could either mix methane with bromine vapor , or bubble the methane through liquid bromine - in either case, exposed to UV light. The original mixture of gases would, of course, be red-brown rather than green. One would not choose to use these reactions as a means of preparing these organic compounds in the lab because the mixture of products would be too tedious to separate. The mechanisms for the reactions are explained on separate pages.

Larger alkanes and chlorine

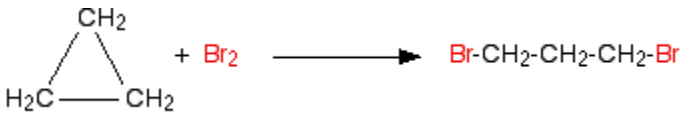
You would again get a mixture of substitution products, but it is worth just looking briefly at what happens if only one of the hydrogen atoms gets substituted (monosubstitution) - just to show that things aren't always as straightforward as they seem! For example, with propane, you could get one of two isomers:



If chance was the only factor, you would expect to get three times as much of the isomer with the chlorine on the end. There are 6 hydrogens that could get replaced on the end carbon atoms compared with only 2 in the middle. In fact, you get about the same amount of each of the two isomers. If you use bromine instead of chlorine, the great majority of the product is where the bromine is attached to the center carbon atom.

Cycloalkanes

The reactions of the cycloalkanes are generally just the same as the alkanes, with the exception of the very small ones - particularly cyclopropane. In the presence of UV light, cyclopropane will undergo substitution reactions with chlorine or bromine just like a non-cyclic alkane. However, it also has the ability to react in the dark. In the absence of UV light, cyclopropane can undergo addition reactions in which the ring is broken. For example, with bromine, cyclopropane gives 1,3-dibromopropane.



This can still happen in the presence of light - but you will get substitution reactions as well. The ring is broken because cyclopropane suffers badly from ring strain. The bond angles in the ring are 60° rather than the normal value of about 109.5° when the carbon makes four single bonds. The overlap between the atomic orbitals in forming the carbon-carbon bonds is less good than it is normally, and there is considerable repulsion between the bonding pairs. The system becomes more stable if the ring is broken.

Contributors and Attributions

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27.8: Polymers and Polymerization Reactions

Prior to the early 1920's, chemists doubted the existence of molecules having molecular weights greater than a few thousand. This limiting view was challenged by Hermann Staudinger, a German chemist with experience in studying natural compounds such as rubber and cellulose. In contrast to the prevailing rationalization of these substances as aggregates of small molecules, Staudinger proposed they were made up of **macromolecules** composed of 10,000 or more atoms. He formulated a **polymeric** structure for rubber, based on a repeating isoprene unit (referred to as a monomer). For his contributions to chemistry, Staudinger received the 1953 Nobel Prize. The terms **polymer** and **monomer** were derived from the Greek roots poly (many), mono (one) and meros (part).

Recognition that polymeric macromolecules make up many important natural materials was followed by the creation of synthetic analogs having a variety of properties. Indeed, applications of these materials as fibers, flexible films, adhesives, resistant paints and tough but light solids have transformed modern society. Some important examples of these substances are discussed in the following sections.

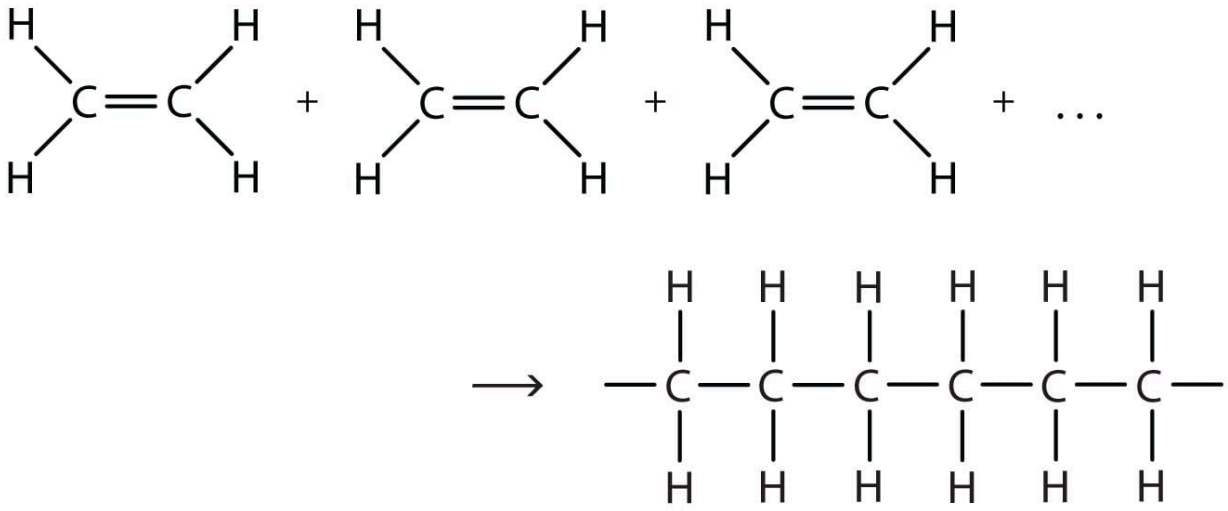
There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers. Ethylene molecules are joined together in long chains.

Note

Many natural materials—such as proteins, cellulose and starch, and complex silicate minerals—are polymers. Artificial fibers, films, plastics, semisolid resins, and rubbers are also polymers. More than half the compounds produced by the chemical industry are synthetic polymers.

Chain-Reaction (Addition) Polymerization

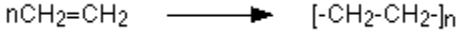
The polymerization can be represented by the reaction of a few monomer units:



The bond lines extending at the ends in the formula of the product indicate that the structure extends for many units in each direction. Notice that all the atoms—two carbon atoms and four hydrogen atoms—of each monomer molecule are incorporated into the polymer structure. Because displays such as the one above are cumbersome, the polymerization is often abbreviated as follows:

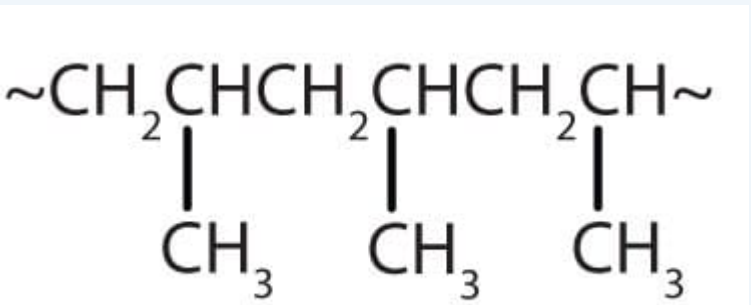
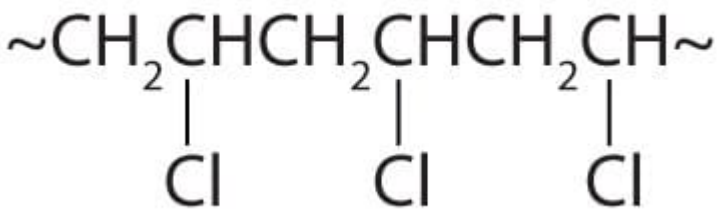
$$n CH_2=CH_2 \rightarrow [-CH_2CH_2-]_n$$

During the polymeriation of ethene, thousands of ethene molecules join together to make poly(ethene) - commonly called polythene. The reaction is done at high pressures in the presence of a trace of oxygen as an initiator.



Some common addition polymers are listed in Table 27.8.1. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table 27.8.1 : Some Addition Polymers

Monomer	Polymer	Polymer Name	Some Uses
$CH_2=CH_2$	~$CH_2CH_2CH_2CH_2CH_2CH_2$~	polyethylene	plastic bags, bottles, toys, electrical insulation
$CH_2=CHCH_3$		polypropylene	carpeting, bottles, luggage, exercise clothing
$CH_2=CHCl$		polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$CF_2=CF_2$	~$CF_2CF_2CF_2CF_2CF_2CF_2$~	polytetrafluoroethylene	nonstick coatings, electrical insulation

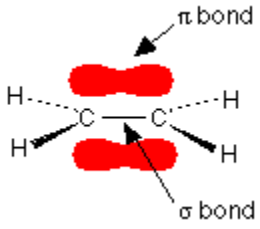
Step 1: Chain Initiation

The oxygen reacts with some of the ethene to give an organic peroxide. Organic peroxides are very reactive molecules containing oxygen-oxygen single bonds which are quite weak and which break easily to give free radicals. You can short-cut the process by adding other organic peroxides directly to the ethene instead of using oxygen if you want to. The type of the free radicals that start the reaction off vary depending on their source. For simplicity we give them a general formula: $Ra^{\bullet}$

Step 2: Chain Propagation

In an ethene molecule, $CH_2=CH_2$, the two pairs of electrons which make up the double bond aren't the same. One pair is held

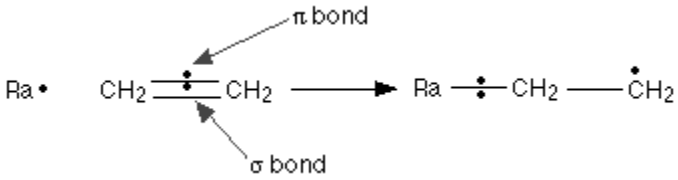
securely on the line between the two carbon nuclei in a bond called a sigma bond. The other pair is more loosely held in an orbital above and below the plane of the molecule known as a π bond.



Note

It would be helpful - but not essential - if you read about the structure of ethene before you went on. If the diagram above is unfamiliar to you, then you certainly ought to read this background material.

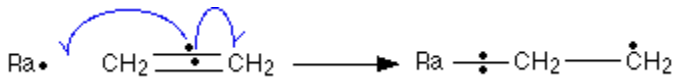
Imagine what happens if a free radical approaches the π bond in ethene.



Note

Don't worry that we've gone back to a simpler diagram. As long as you realise that the pair of electrons shown between the two carbon atoms is in a π bond - and therefore vulnerable - that's all that really matters for this mechanism.

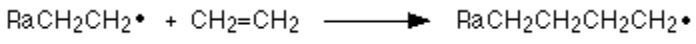
The sigma bond between the carbon atoms isn't affected by any of this. The free radical, Ra•, uses one of the electrons in the π bond to help to form a new bond between itself and the left hand carbon atom. The other electron returns to the right hand carbon. You can show this using "curly arrow" notation if you want to:



Note

If you aren't sure about about curly arrow notation you can follow this link.

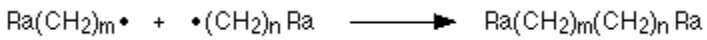
This is energetically worth doing because the new bond between the radical and the carbon is stronger than the π bond which is broken. You would get more energy out when the new bond is made than was used to break the old one. The more energy that is given out, the more stable the system becomes. What we've now got is a bigger free radical - lengthened by CH_2CH_2. That can react with another ethene molecule in the same way:



So now the radical is even bigger. That can react with another ethene - and so on and so on. The polymer chain gets longer and longer.

Step 3: Chain Termination

The chain does not, however, grow indefinitely. Sooner or later two free radicals will collide together.

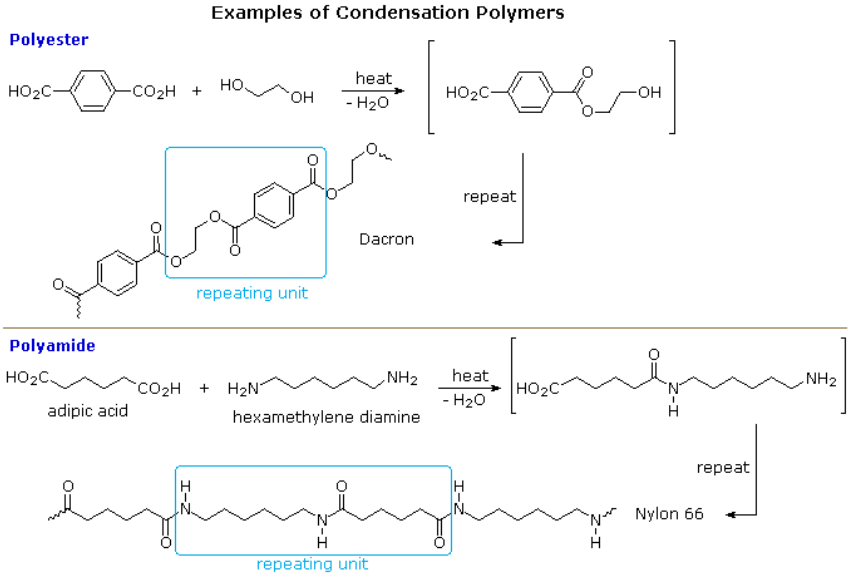


That immediately stops the growth of two chains and produces one of the final molecules in the poly(ethene). It is important to realise that the poly(ethene) is going to be a mixture of molecules of different sizes, made in this sort of random way. Because chain termination is a random process, poly(ethene) will be made up of chains of different lengths.

Step-Reaction (Condensation) Polymerization

A large number of important and useful polymeric materials are not formed by chain-growth processes involving reactive species such as radicals, but proceed instead by conventional functional group transformations of polyfunctional reactants. These polymerizations often (but not always) occur with loss of a small byproduct, such as water, and generally (but not always) combine two different components in an alternating structure. The polyester Dacron and the polyamide Nylon 66, shown here, are two examples of synthetic condensation polymers, also known as step-growth polymers. In contrast to chain-growth polymers, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbon-heteroatom bond formation (C-O & C-N in Dacron & Nylon respectively). Although polymers of this kind might be considered to be alternating copolymers, the repeating monomeric unit is usually defined as a combined moiety.

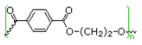
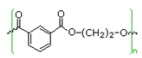
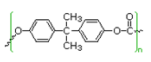
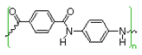
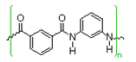
Examples of naturally occurring condensation polymers are cellulose, the polypeptide chains of proteins, and poly(β-hydroxybutyric acid), a polyester synthesized in large quantity by certain soil and water bacteria. Formulas for these will be displayed below by clicking on the diagram.



Characteristics of Condensation Polymers

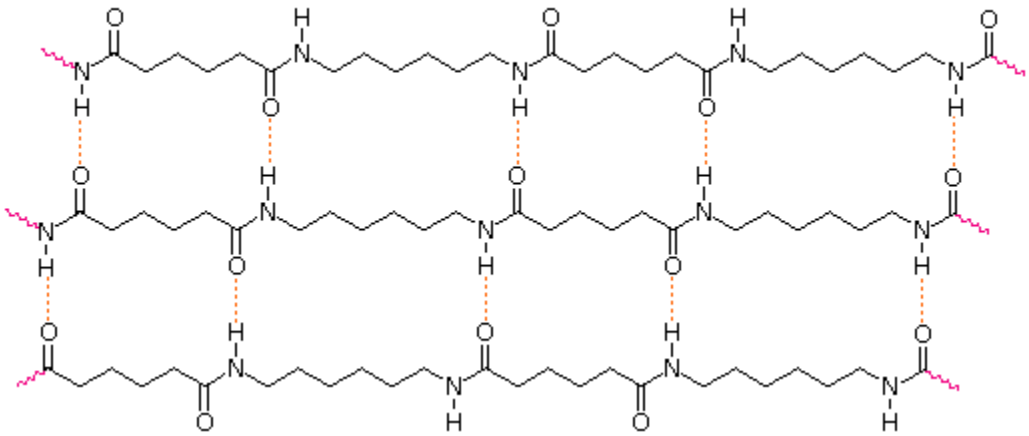
Condensation polymers form more slowly than addition polymers, often requiring heat, and they are generally lower in molecular weight. The terminal functional groups on a chain remain active, so that groups of shorter chains combine into longer chains in the late stages of polymerization. The presence of polar functional groups on the chains often enhances chain-chain attractions, particularly if these involve hydrogen bonding, and thereby crystallinity and tensile strength. The following examples of condensation polymers are illustrative.

Note that for commercial synthesis the carboxylic acid components may actually be employed in the form of derivatives such as simple esters. Also, the polymerization reactions for Nylon 6 and Spandex do not proceed by elimination of water or other small molecules. Nevertheless, the polymer clearly forms by a step-growth process. Some Condensation Polymers

Formula	Type	Components	T_g °C	T_m °C
~[CO(CH$_2$)$_4$CO-OCH$_2$CH$_2$O]$_n$~	polyester	HO$_2$C-(CH$_2$)$_4$-CO$_2$H HO-CH$_2$CH$_2$-OH	< 0	50
	polyester Dacron, Mylar	para HO$_2$C-C$_6$H$_4$-CO$_2$H HO-CH$_2$CH$_2$-OH	70	265
	polyester	meta HO$_2$C-C$_6$H$_4$-CO$_2$H HO-CH$_2$CH$_2$-OH	50	240
	polyester Lexan	(HO-C$_6$H$_4$-)$_2$C(CH$_3$)$_2$ (Bisphenol A) X$_2$C=O (X = OCH$_3$ or Cl)	150	267
~[CO(CH$_2$)$_4$CO-NH(CH$_2$)$_6$NH]$_n$~	polyamide Nylon 66	HO$_2$C-(CH$_2$)$_4$-CO$_2$H H$_2$N-(CH$_2$)$_6$-NH$_2$	45	265
~[CO(CH$_2$)$_5$NH]$_n$~	polyamide Nylon 6 Perlon		53	223
	polyamide Kevlar	para HO$_2$C-C$_6$H$_4$-CO$_2$H para H$_2$N-C$_6$H$_4$-NH$_2$	---	500
	polyamide Nomex	meta HO$_2$C-C$_6$H$_4$-CO$_2$H meta H$_2$N-C$_6$H$_4$-NH$_2$	273	390

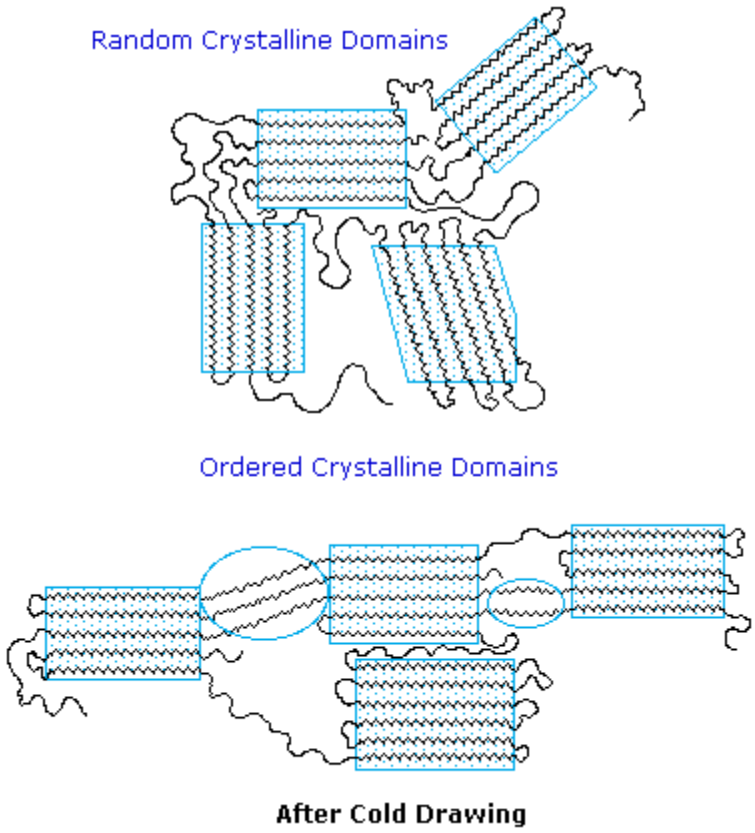
The difference in Tg and Tm between the first polyester (completely aliphatic) and the two nylon polyamides (5th & 6th entries) shows the effect of intra-chain hydrogen bonding on crystallinity. The replacement of flexible alkylidene links with rigid benzene rings also stiffens the polymer chain, leading to increased crystalline character, as demonstrated for polyesters (entries 1, 2 &3) and polyamides (entries 5, 6, 7 & 8). The high Tg and Tm values for the amorphous polymer Lexan are consistent with its brilliant transparency and glass-like rigidity. Kevlar and Nomex are extremely tough and resistant materials, which find use in bullet-proof vests and fire resistant clothing.

Interchain Hydrogen Bonding Enhances Crystallinity

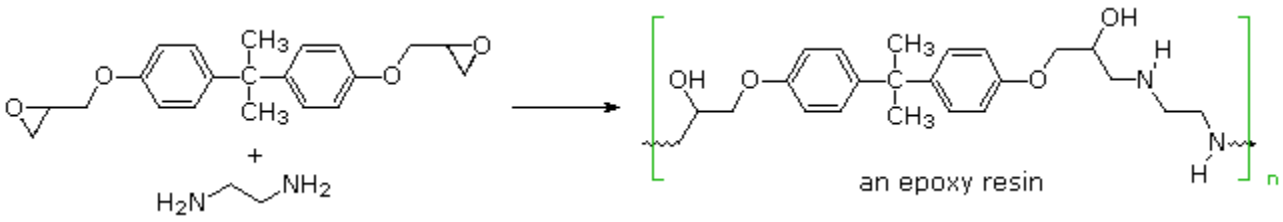


Many polymers, both addition and condensation, are used as fibers The chief methods of spinning synthetic polymers into fibers are from melts or viscous solutions. Polyesters, polyamides and polyolefins are usually spun from melts, provided the Tm is not too high. Polyacrylates suffer thermal degradation and are therefore spun from solution in a volatile solvent. Cold-drawing is an important physical treatment that improves the strength and appearance of these polymer fibers. At temperatures above T_g, a thicker than desired fiber can be forcibly stretched to many times its length; and in so doing the polymer chains become untangled, and tend to align in a parallel fashion. This cold-drawing procedure organizes randomly oriented crystalline domains, and also aligns amorphous domains so they become more crystalline. In these cases, the physically oriented morphology is stabilized and retained in the final product. This contrasts with elastomeric polymers, for which the stretched or aligned morphology is unstable relative to the amorphous random coil morphology.

This cold-drawing treatment may also be used to treat polymer films (e.g. Mylar & Saran) as well as fibers.



Step-growth polymerization is also used for preparing a class of adhesives and amorphous solids called epoxy resins. Here the covalent bonding occurs by an S_N2 reaction between a nucleophile, usually an amine, and a terminal epoxide. In the following example, the same bisphenol A intermediate used as a monomer for Lexan serves as a difunctional scaffold to which the epoxide rings are attached. Bisphenol A is prepared by the acid-catalyzed condensation of acetone with phenol.



Contributors and Attributions

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- Jim Clark (Chemguide.co.uk)

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27.9: Synthesis of Organic Compounds

Wöhler synthesis of Urea in 1828 heralded the birth of modern chemistry. The Art of synthesis is as old as Organic chemistry itself. Natural product chemistry is firmly rooted in the science of degrading a molecule to known smaller molecules using known chemical reactions and conforming the assigned structure by chemical synthesis from small, well known molecules using well established synthetic chemistry techniques. Once this art of synthesizing a molecule was mastered, chemists attempted to modify bioactive molecules in an attempt to develop new drugs and also to unravel the mystery of biomolecular interactions. Until the middle of the 20th Century, organic chemists approached the task of synthesis of molecules as independent tailor made projects, guided mainly by chemical intuition and a sound knowledge of chemical reactions. During this period, a strong foundation was laid for the development of mechanistic principles of organic reactions, new reactions and reagents. More than a century of such intensive studies on the chemistry of carbohydrates, alkaloids, terpenes and steroids laid the foundation for the development of logical approaches for the synthesis of molecules.

The job of a synthetic chemist is akin to that of an architect (or civil engineer). While the architect could actually see the building he is constructing, a molecular architect called Chemist is handicapped by the fact that the molecule he is synthesizing is too small to be seen even through the most powerful microscope developed to date. With such a limitation, how does he 'see' the developing structure? For this purpose, a chemist makes use of spectroscopic tools. How does he cut, tailor and glue the components on a molecule that he cannot see? For this purpose chemists have developed molecular level tools called Reagents and Reactions. How does he clean the debris and produce pure molecules? This feat is achieved by crystallization, distillation and extensive use of Chromatography techniques. A mastery over several such techniques enables the molecular architect (popularly known as organic chemist) to achieve the challenging task of synthesizing the mirade molecular structures encountered in Natural Products Chemistry, Drug Chemistry and modern Molecular Materials. In this task, he is further guided by several 'thumb rules' that chemists have evolved over the past two centuries. The discussions on the topics **Name Reactions, Reagents** for synthesis, **Spectroscopy** and **Chromatography** are beyond the scope of this write-up. Let us begin with a brief look at some of the important ***'Rules'*** *in organic chemistry that guide us in planning organic synthesis.* We would then discuss Protection and Deprotection of some important functional groups. We could then move on to the Logic of planning Organic Synthesis.

Modern Synthesis

A multi-step synthesis of any organic compound requires the chemist to accomplish three related tasks:

1. Constructing the carbon framework or skeleton of the desired molecule.
2. Introducing, removing or transforming functional groups in a fashion that achieves the functionality of the desired compound.
3. Exercising selective stereocontrol at all stages in which centers of stereoisomerism are created or influenced. These are not discrete independent tasks to be attacked and solved in turn, but must be integrated and correlated in an overall plan. Thus, the assembly of the molecular framework will depend in part on the structure and functionality of available starting materials, the selectivity (regio and stereo) of the various reactions that may be used to stitch them together, and the loss or relocation of functional groups in the intermediate compounds formed on the way to the final product.

Other factors must also be considered, always in context with those listed above:

4. Since a successful synthesis must produce the desired product in reasonable amount, it should be as short and efficient as possible. A two or three-step sequence is usually better than a six or seven step procedure, even if the individual step yields are better in the longer route. Most reactions do not proceed in 100% yield, and the losses are multiplied with each additional step. Furthermore, a long multi-step synthesis requires many hours of effort by the chemists conducting the reactions.
5. The format of a synthesis is important. Assuming a constant yield for each step, a linear sequence of reactions gives a poorer overall yield than the same number of convergent reactions, as shown in the following diagram.
6. If numerous functional groups are present at intermediate stages, some of these may require protection from unwanted reaction. Since the use of a protective group requires its introduction and later removal, such operations can add many steps to a synthesis. A similar cost is attached to the use of blocking and activating groups.
7. The starting compounds and reagents for a synthesis must be purchased, so economic considerations are often significant. Recovery or recycling of expensive reagents and catalysts is often desirable. Also, if large amounts of useless by-products are formed in the synthesis, the expense of their disposal is a factor. The term atom efficiency has been coined to reflect the latter point.
8. For a given target molecule, several different reaction sequences may serve to accomplish its synthesis. Indeed, new

synthetic routes to known compounds continue to be reported, particularly as new reactions are developed and applied to difficult transformations. Evaluating the quality and efficacy of these diverse procedures involves consideration of all the above. Over the course of the past hundred years, a very large number of syntheses for a wide variety of compounds have been recorded. For all but the simplest of these, a majority of the reactions in the synthesis involve functional group modification, preceding or following a smaller number of carbon-carbon bond forming reactions. Because functional group chemistry consists of such a vast number of addition, elimination and substitution interconversions, it is not possible to identify a general pattern in their application to synthesis. Instead, an example from the synthesis of reserpine by the R. B. Woodward group (Harvard), displayed in the following diagram, will serve to illustrate the importance of regio and stereo-control in the course of functional group modification.

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28: CHEMISTRY OF THE LIVING STATE

Petrucci: *General Chemistry*
Principles and Modern Applications

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- Topic hierarchy

28.1: Chemical Structure of Living Matter: An Overview
28.2: Lipids
28.3: Carbohydrates
28.4: Proteins
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28.6: Nucleic Acids

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28.1: Chemical Structure of Living Matter: An Overview

Learning Objectives

- To identify the common structural units of important biological molecules.

Contributors

- Anonymous

Modified by Joshua B. Halpern

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